Dynamical Nucleation Theory: A New Molecular Approach to Vapor-Liquid Nucleation

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A new theoretical approach is presented for vapor-phase nucleation. In contrast to previous molecular approaches to nucleation that focus on evaluating equilibrium distributions of clusters, we evaluate rate constants for cluster evaporation and condensation that are the elementary kinetic steps in the nucleation mechanism. The use of variational transition state theory to estimate the rate constants provides a consistent procedure for defining a unique value for the constraining volume of the physically consistent cluster. The theory is applied to evaporation of small water clusters. [S0031-9007(99)08965-6]

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The condensation of liquid drops from vapor phase molecules plays an important role in atmospheric processes. Because of the importance of nucleation phenomena and the need to accurately model these processes, considerable effort has been made to develop theoretical approaches that can accurately predict nucleation rates. Classical nucleation theory (CNT) [1] is the most widely used theory for describing homogeneous nucleation. CNT is approximate and where agreement between experiment and CNT is observed, it is usually within a narrow range of saturation ratios and temperatures. Theoretical consideration also shows CNT provides the correct value of this slope, but not the absolute value of nucleation rate [2]. Although many extensions and modifications have been made to the theory (see the review by Laaksonen, Talanquer, and Oxtoby [3]), these changes have not led to a general theory that is applicable and reliable for a variety of systems. Promising alternatives to CNT are offered by microscopic approaches. The goal of molecular theories is to obtain nucleation rates starting from the potential energy of interaction between molecules. One general approach is to employ molecular simulations to evaluate properties of isolated clusters, such as the free energy of forming the cluster, which can be used to approximate nucleation rates [4–10]. As with CNT, the molecular approaches presented to date have not resulted in a general theory that is routinely applied to calculate nucleation rates for systems of interest.

For the molecular approaches referred to above (as well as CNT), the central quantity needed to calculate the nucleation rate is the free energy for cluster formation. It is worthwhile to examine the approximations inherent in these molecular approaches. The starting point for the molecular approaches is the assumption that addition and removal of monomers from clusters adequately describes the nucleation kinetics, e.g.,

$$N_1 + N_{i-1} \underset{\alpha_i}{\overset{\beta_{i-1}}{\rightleftarrows}} N_i, \qquad i = 1, 2, \ldots, \tag{1}$$

where N_1 is the number of monomers, N_i $(i > 1)$ is the number of clusters containing i monomers, and α_i and β_i are evaporation and condensation rate constants, respectively. The nucleation rate is obtained by solving the pseudo-first-order kinetic equations (assuming N_1 is large and constant)

$$\frac{dN_i}{dt} = \beta_{i-1}N_{i-1} - \alpha_i N_i - \beta_i N_i + \alpha_{i+1}N_{i+1}. \tag{2}$$

The first major approximation is that the condensation rate constant can be approximated by the collision rate of monomers with the cluster, $\beta_i = (\overline{c}/4)(4\pi r_i^2)\rho_1$. The average speed of the monomers in the gas phase is $\overline{c} = (8k_BT/\pi m)^{1/2}$, ρ_1 is the monomer density, k_B is Boltzmann's constant, T is temperature, and m is the monomer mass. This expression for the condensation rate constant approximates the cross section for collisions by the surface area of a sphere of radius r_i and assumes unit sticking probability upon collision. The evaporation rate constant is then evaluated using detailed balance $\alpha_i = \beta_{i-1}(N_{i-1}^{\mathrm{eq}}/N_i^{\mathrm{eq}})$, where N_i^{eq} is the equilibrium cluster distribution. The task then reduces to evaluating N_i^{eq}, or equivalently the free energies, for forming the clusters from monomers. Molecular approaches employ statistical mechanics to evaluate N_i^{eq}. Because the clusters that are important in the nucleation process can dissociate, the cluster distributions diverge as the volume containing the cluster increases. This type of behavior has been clearly demonstrated in the volume dependence of the free energy of cluster formation in the seminal work by Lee, Barker, and Abraham [5]. Treatment of the volume dependence of this free energy has been a source of confusion and controversy in the development of a general molecular theory of nucleation.

In the present Letter, we present a new molecular theory of nucleation in which the evaporation and condensation rate constants are *directly* calculated. This approach has two major advantages over the previous molecular approaches. First, the direct evaluation of the rate constants avoids approximating the condensation rate constant using a simple gas collision rate. Second, the formulation of the rate constant naturally yields a consistent prescription for dealing with the volume dependence of the free energy for cluster formation and actually exploits this dependence. In the remainder of this paper, we outline the theory and present preliminary calculations on water clusters. A more rigorous derivation of the rate constant expressions will be presented elsewhere [11].

We view the processes of evaporation and condensation as gas-phase dissociation and association reactions. This view of nucleation as a gas-phase reaction mechanism composed of dissociation and association reactions is quite different than the perspective generally encountered where nucleation is viewed as density fluctuations in a supersaturated fluid. Given the large distance between water monomers and clusters in the vapor ($>10^4$ Å for water at a supersaturation of 5), the view of nucleation as a gas-phase reaction mechanism is quite reasonable. Transition state theory (TST) [12] provides a convenient framework to evaluate equilibrium rate constants for these kinetic processes. For the barrierless dissociation reaction considered here, quantum tunneling effects will be negligible, and quantum effects will be important only for bound vibrational motions. We treat the molecules as rigid and assume that a classical statistical mechanics description of the intermolecular motion is adequate. This is a reasonable first-order approximation for the system studied here, and it is consistent with the fact that the potential that we use has been parametrized using classical statistical mechanics. This assumption will be tested in the future using Feynman path integral methods [13].

The TST rate constant is approximated by the equilibrium one-way flux through a dividing surface separating reactants from products. For evaporation of a monomer from an i-molecule cluster, reactants are an i-molecule cluster and products are a monomer infinitely separated from an $(i-1)$-molecule cluster. In the present work, we choose the dividing surface to be a sphere with its center at the center of mass of the i-molecule cluster; the radius of the sphere then determines the location of the dividing surface. (Spherical dividing surfaces are chosen to make contact with previous work that used spherical constraining volumes as well as the simplicity they lend to the theory. Studies of alternate dividing surfaces and classical recrossing factors are planned for the future.) For the dissociation reaction studied here, the location of the dividing surface is guided by variational TST (VTST) [12,14–16]. The fundamental dynamical assumption of TST [17] guarantees that the TST approximation to the classical reactive flux is greater than or equal to the exact classical flux. This upper bound is the basis for variational TST in which the transition state dividing surface is located to minimize the reactive flux. Thus, VTST gives a prescription for defining a unique location of the dividing surface (or radius of the sphere) for each reaction.

For simplicity, we present the theory for the nucleation of atoms (e.g., rare gas atoms), although extension to include internal and rotational degrees of freedom is straightforward. The dividing surface for evaporation of an i-molecule cluster is defined by $S_i(\mathbf{r}^{(i)}, r) = 0$, where the coordinates of the system $\mathbf{r}^{(i)} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i)$ are the collection of three-dimensional Cartesian coordinates for each atom, and r is the parameter defining the radius of the spherical dividing surface. For the spherical dividing surface, the following relation implicitly defines the function S_i

$$\theta(S_i) = \prod_{j=1}^{i} \theta(r - |\mathbf{r}_j - \mathbf{R}_i|), \tag{3}$$

where $\theta(x)$ is the Heaviside step function $[\theta(x) = 0, x < 0; \theta(x) = 1, x > 0]$, and $\mathbf{R}_i = (1/i)\sum_{j=1}^{i} \mathbf{r}_j$ is the center of mass of the i-molecule cluster. Using the classical TST rate constant expression for a general dividing surface [15], the generalized TST rate constant for evaporation of the i-molecule cluster is written

$$q_i^R(T,r)\alpha_i^{\mathrm{GT}}(T,r) = \frac{1}{i!\,h^{3i}} \int d\mathbf{p}^{(i)} \int d\mathbf{r}^{(i)} \exp\left[-\frac{H_i(\mathbf{p}^{(i)},\mathbf{r}^{(i)})}{k_B T}\right] \frac{1}{2} \left| \frac{\partial\theta[S(\mathbf{r}^{(i)},r)]}{\partial \mathbf{r}^{(i)}} \cdot \frac{\mathbf{p}^{(i)}}{m} \right|, \tag{4}$$

where $\mathbf{p}^{(i)}$ are momenta conjugate to $\mathbf{r}^{(i)}$, H_i is the Hamiltonian for the cluster, and h is Planck's constant. The reactant partition function $q_i^R(T,r)$ is given by

$$\begin{aligned} q_i^R(T,r) &= \frac{1}{i!\,h^{3i}} \int d\mathbf{p}^{(i)} \int d\mathbf{r}^{(i)} \exp\left[-\frac{H_i(\mathbf{p}^{(i)},\mathbf{r}^{(i)})}{k_B T}\right] \theta[S(\mathbf{r}^{(i)},r)] \\ &= \frac{\gamma^i}{i!} \int d\mathbf{r}^{(i)} \exp\left[-\frac{U_i(\mathbf{r}^{(i)})}{k_B T}\right] \prod_{j=1}^{i} \theta(r - |\mathbf{r}_j - \mathbf{R}_i|), \end{aligned} \tag{5}$$

where $\gamma = (2\pi m k_B T/h^2)^{3/2}$, and U_i is the interaction potential. This definition of the reactant partition function is equivalent to expressions that have appeared in previous work [4–6] where the partition function is related to the total Helmholtz free energy for forming the cluster from monomers by $A_i(T,r) = -k_B T \ln[q_i^R(T,r)]$.

The evaporation rate constant in Eq. (4) can be recast into the more traditional form of a ratio of partition functions [16]

$$\alpha_i^{\mathrm{GT}}(T,r) = \frac{k_B T}{h} \frac{q_i^{\mathrm{GT}}(T,r)}{q_i^R(T,r)}, \tag{6}$$

where the generalized transition state partition function $q_i^{\mathrm{GT}}(T,r)$ is [11]

$$q_i^{\mathrm{GT}}(T,r) = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \frac{\gamma^i}{i!} \int d\mathbf{r}^{(i)} \exp\left[-\frac{U_i(\mathbf{r}^{(i)})}{k_B T}\right] \times \sum_{k=1}^{i} \delta(r - |\mathbf{r}_k - \mathbf{R}_i|) \prod_{j \neq k}^{i} \theta(r - |\mathbf{r}_j - \mathbf{R}_i|). \tag{7}$$

The zero of energy for the two partition functions is chosen to be the same, so the Boltzmann factor that is normally present in the traditional TST expression is not explicitly included. The Dirac delta function $\delta(x)$ in Eq. (7) constrains the system to lie on the dividing surface; i.e., one of the molecules is constrained to the surface of the sphere. This constrained ensemble is the same as the "shell-molecule ensemble" [7], with the modification of Ellerby [9] that the shell molecule interacts with the other molecules in the cluster. However, the relationship between the partition function for this constrained ensemble and the evaporation rate constant is a *unique* contribution of the present work.

The TST approximation to the reactive flux through the dividing surface, $q_i^R(T,r)\alpha_i^{\mathrm{GT}}(T,r) = (k_B T/h) q_i^{\mathrm{GT}}(T,r)$, is an upper bound to the exact classical reactive flux. The minimum value of the reactive flux is found by variationally optimizing the location of the dividing surface, which in this case is determined by the radius r of the sphere constraining the cluster. The VTST rate constant is given by

$$q_i^R(T,r_i^\ddagger)\alpha_i^{\mathrm{VTST}}(T) = \min_r \left\{\frac{k_B T}{h} q_i^{\mathrm{GT}}(T,r)\right\} = \frac{k_B T}{h} q_i^{\mathrm{GT}}(T,r_i^\ddagger), \tag{8}$$

where $r_i^\ddagger$ is the location that minimizes the reactive flux. Comparing the expressions for the reactant and transition state partition functions, Eqs. (5) and (7), it is easy to show that they are related by

$$q_i^{\mathrm{GT}}(T,r) = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \frac{d}{dr} q_i^R(T,r) = -\left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \frac{q_i^R(T,r)}{k_B T} \frac{d}{dr} A_i(T,r). \tag{9}$$

Thus, the VTST expression for the evaporation rate constant takes on the appealing form

$$\alpha_i^{\mathrm{VTST}}(T) = -\left(\frac{1}{2\pi m k_B T}\right)^{1/2} \frac{d}{dr} A_i(T,r)\Big|_{r=r_i^\ddagger} = \frac{\bar{c}}{4}\,[4\pi(r_i^\ddagger)^2]\,\frac{P_i^{\mathrm{int}}}{k_B T}, \tag{10}$$

where the internal pressure of the i-molecule cluster is defined by $P_i^{\mathrm{int}} = -dA_i(T,r)/dv|_{r=r_i^\ddagger}$ and $v = 4\pi r^3/3$. Equation (10) is the central result of this Letter. This expression points out the importance of knowing the dependence of the Helmholtz free energy on the radius r. Unlike some previous studies that assume the Helmholtz free energy is relatively insensitive to variations of r, we see that *it is crucial to know how $A_i(T,r)$ varies with r* since this dependence determines the rate constant. In addition, the formulation presented here gives for the first time a fundamentally justified prescription for choosing the optimum value of r for each cluster. This prescription selects those clusters that are the most stable relative to evaporation, since the reactive flux is a minimum for the optimum choice of constraining volume.

In this Letter we have described the first steps in defining a dynamical nucleation theory. A complete dynamical nucleation theory requires specification of the condensation rate constants β_{i-1} and a prescription for solution of the kinetic equations in Eq. (2). These steps will be described in detail in subsequent publications. It should be noted that TST obeys microscopic reversibility, so that the reactive flux for the condensation process of a monomer in an $(i-1)$ molecule cluster is the same as the reactive flux for the evaporation of the i-molecule cluster. Determination of the condensation rate constant β_{i-1} requires evaluation of the correct normalization factor (the reactant partition function) for the condensation process.

We demonstrate the method by calculating the evaporation rate constants for water clusters. Monte Carlo techniques are used to evaluate the configurational integral in Eq. (5) for the reactant partition function, and the

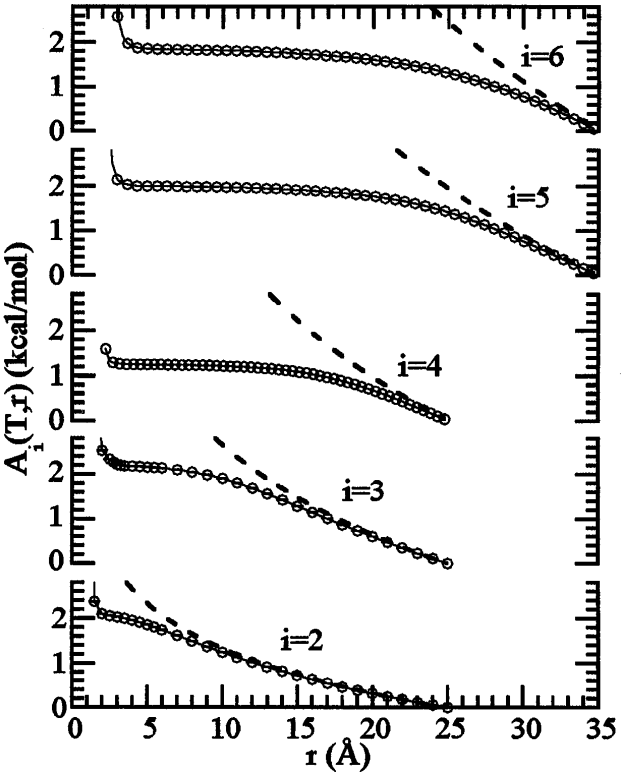

FIG. 1. Dependence of the total Helmholtz free energy $A_i(T,r)$ on the radius of the constraining volume for i-molecule water clusters at 243 K. Solid lines with symbols are the simulation results and dashed lines are the analytical results for a cluster of noninteracting molecules (ideal gas). The zero of energy for each curve is arbitrary.

TABLE I. Cluster radius $r_i^{\ddagger}$, VTST evaporation rate constant $\alpha_i^{\mathrm{VTST}}(T)$, and internal pressure P_i^{int}, of i-molecule water clusters at 243 K.

i	$r_i^{\ddagger}$ (Å)	α_i^{VTST} (s^{-1})	P_i^{int} (atm)
2	2.8	1.6×10^{11}	43
3	4.3	4.8×10^{10}	5.3
4	5.8	4.7×10^{9}	0.28
5	5.8	1.0×10^{10}	0.60
6	6.3	1.3×10^{10}	0.64

evaporation rate constants are obtained using Eq. (10). Details of the simulation technique will be given elsewhere [11]. The polarizable water potential of Dang and Chang [18] is used in the simulations. Figure 1 presents the total Helmholtz free energies for forming clusters containing 2–6 water molecules at 243. Only the derivative $dA_i(T,r)/dr$ is needed for computing rate constants, not absolute values of $A_i(T,r)$. Therefore, the zero of energy for each cluster is arbitrarily set. The figure also includes the analytical results [5] for noninteracting molecules. In all cases, $A_i(T,r)$ is a monotonically decreasing function of r. For the water dimer and trimer, $A_i(T,r)$ shows strong dependence on r over the entire range of r, but it is still possible to determine where $dA_i(T,r)/dr$ has a minimum. The free energy curves for the larger clusters at 243 K do show regions of relative insensitivity to r. However, as stated above, the slope of $A_i(T,r)$ is crucial since it determines the rate constant. In addition, we expect that at higher temperatures the $A_i(T,r)$ curves will show stronger dependence on r. Studies of the temperature dependence are currently underway as well as extensions of the calculations to larger clusters.

Table I presents the optimum value of the radius, the evaporation rate constants, and the internal pressures for the clusters. As the number of molecules in the cluster increases from 2 to 4, the radius of the constraining sphere grows with increasing cluster size and the evaporation rate constant and internal pressure drop dramatically. More complex size dependence of cluster radii, evaporation rate constants, and internal pressures are seen in going to the larger clusters. To understand these trends, further studies are under way to characterize the structure and thermochemistry of these clusters and larger ones.

In summary, a new theoretical approach to vapor-phase nucleation has been developed that directly evaluates the relevant dynamical quantities rather than focusing on equilibrium properties of clusters. Variational transition state theory is used to obtain expressions for the equilibrium rate constants. We choose a TST dividing surface that is equivalent to the surface of the constraining volume defining “physically consistent clusters” of Reiss and co-workers [4,6]. In the present work, the variational procedure locates the dividing surface that minimizes the reactive flux, thereby defining a unique volume for each cluster. This is the first time that the cluster volume has been uniquely defined based upon fundamental considerations. The resulting rate constant expression is proportional to the derivative, with respect to v, of the Helmholtz free energy for forming the cluster. In contrast to previous assertions that the Helmholtz free energy is relatively insensitive to the constraining volume (for reasonable choices of v), we find that the sensitivity to v is crucial since this dependence determines the rate constant.

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