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THEORY OF NUCLEATION OF WATER
PROPERTIES OF SOME CLATHRATE LIKE CLUSTER STRUCTURES

by

MEHDI DAEE, 1940-

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ABSTRACT

The tranquility of classical homogeneous nucleation theory has been disturbed by the introduction of statistical mechanical correction factors to a basically thermodynamic theory. These factors, which appear to be essential, destroy much of the agreement with experiment in the case of water vapor. A molecular model for the pre-nucleation water clusters is proposed with a view toward resolving some of these difficulties. As a first step, the properties of a few specific cluster configurations have been examined. Clathrate-like structures containing 16 to 57 water molecules are discussed. The hydrogen bonds were treated as simple harmonic oscillators for the purpose of calculating normal mode frequencies. The Helmholtz free energy of formation of the cluster is calculated from the appropriate partition functions. For these clathrate-like structures the free energy of formation was not found to be a smoothly increasing function of the number of molecules but showed minima corresponding to close cages.

INTRODUCTION

It is not uncommon for aerosols to be formed by the nucleation of particles from a supersaturated vapor. Nucleation may either be homogeneous or heterogeneous. In the former, a relatively high supersaturation is required to enhance heterophase fluctuations (1) which are responsible for the formation of large molecular clusters. Some of these clusters will become free growing once they pass a certain size called the critical size. In the case of heterogeneous nucleation, clustering takes place on the surface of macroscopic particles, collections of which already exist as an aerosol. In this case the presence of the foreign particle greatly reduces the height of the nucleation barrier so that the formation of free growing clusters can proceed at a lower supersaturation. A detailed understanding of homogeneous nucleation is a necessary prerequisite for studying heterogeneous nucleation. In this paper we discuss only homogeneous nucleation.

The classical theory of homogeneous nucleation, developed by Volmer and Flood (2), Farkas (3), Becker and Doring (4), Zeldovich (5) and Frenkel (6) is based on the semiphenomenological liquid drop model which assumes that bulk concepts (such as bulk latent heat, liquid density and surface tension) can be extended down to clusters composed of a relatively small number of molecules. This theory also assumes that

the supersaturated vapor is composed of a mixture of different size spherical clusters. The distribution of clusters to a good approximation, is assumed to be a mixture of ideal gases with interactions occurring only between the molecules of a given cluster. Following reference (7) we assume that the Helmholtz free energy of a cluster of size g , $A(g)$, can be written as the sum of contributions due to bulk free energy and surface free energy

$$A(g) = g\mu_B + \sigma A(g) \quad [1]$$

where μ_B is the molecular chemical potential of the bulk material if it is at the pressure outside of the droplet, σ is the macroscopic interfacial free energy per unit area and $A(g)$ is the surface area of the cluster of size g . For the isothermal reversible work of formation of a cluster of size g in the midst of the vapor monomer, $\Delta A(g)$, we use the following expressions:

$$\Delta A(g) = A(g) - g\mu_V, \quad [2a]$$

$$\Delta A(g) = g(\mu_B - \mu_V) + \sigma A(g), \quad [2b]$$

where $g\mu_V$ is the free energy of g vapor molecules. Since the supersaturated vapor is not in equilibrium with its bulk,

$$\mu_B - \mu_V = -kT \ln(P/P_\infty) + u_B(P - P_\infty) \quad [3]$$

where P is the pressure of the vapor, P_∞ is the equilibrium vapor pressure over a plane surface at temperature T , k is Boltzmann's constant, and μ_B is the volume per molecule in the bulk liquid phase.

Since the compressibility of the liquid is small, $\mu_B(P-P_\infty)$ can be ignored. $\Delta A(g)$ can be expressed in terms of the supersaturation ratio, $S = P/P_\infty$,

$$\Delta A(g) = -gkT \ln S + \sigma A(g). \quad [4]$$

The above equation is the "classical" expression for the change in the Helmholtz free energy (9) and neglects the $\mu_B(P-P_\infty)$ term and terms representing the free energy of translation and rotation mentioned below. Fig. 1 shows $\Delta A(g)$ as a function of g evaluated at a given temperature, T , and supersaturation, $S > 1$. The concentration of g -mers (7) in equilibrium with the monomers, $C_o(g)$, is given by

$$C_o(g) = C(1) \exp[-\Delta A(g)/kT]. \quad [5]$$

Here the subscript "o" denotes the equilibrium condition.

Fig. 2 shows the behavior of $C_o(g)$ as a function of g . The maximum in $\Delta A(g)$ (found at the point where $d[\Delta A(g)]/dg=0$) defines the critical cluster size, g^* , and the corresponding equilibrium concentration of critical clusters, $C_o(g^*)$. It is convenient to note that $\Delta A(g)$ increases monotonically

up to g^* and thereafter decreases monotonically. Correspondingly, $C_o(g)$ decreases monotonically with increasing g up to g^* . For small systems of asymmetric molecules possessing large interaction potentials, such as water, one would expect structural effects to show up in such functions; however, the semiphenomenological liquid drop model cannot be expected to account for more than just the broad general features of such systems.

There are necessary correction factors which must be added to the above expression for $A(g)$, Eq. [1]. It has been shown by Kiang (27) that a general form for $A(g)$ is as follows:

$$A(g) = gE + \sigma A(1)g^\delta + \tau kT \ln g + \text{const.}$$

This general form is consistent with the work of Lothe and Pound (11), Reiss, Katz and Cohen (28), and Kiang (27). $A(1)$ is the "surface area" of a monomer, and δ is a parameter which allows different geometric shapes for the cluster; for spherical clusters $\delta = 2/3$. On the coexistence curve $E = \mu_B$. The third term is a correction originally suggested by Frenkel (6) and later more fully developed by Lothe and Pound (11). This term is essentially the free energy of translation and rotation which the cluster is able to assume as a rigid body constituent of an ideal gas. Lothe and Pound express the free energy of translation and rotation

per cluster, $A_{T-R}(g)$, as follows:

$$A_{T-R}(g) = -kT \ln[Z_t Z_r]$$

where $Z_t = u [2\pi mkT/h^2]^{3/2} g^{3/2}$

and $Z_r = \pi^{7/2} [8kT/h^2]^{3/2} I^{3/2}$

where m is the mass of the constituent molecule (water in our case), u is the molecular volume, and I , is the moment of inertia of the g cluster. Lothe and Pound add another correction $+kT \ln Z_{rep} \approx 5kT$ which is their estimate of the reduction in entropy which accompanies the deactivation of six degrees of freedom from the embryo's bulk free energy term. For the Lothe-Pound theory $\tau = -4$. The constant term in $A(g)$ includes factors from Z_t and Z_r and, of course, in the general case may represent other unknowns.

The translation-rotation correction factors predict values for nucleation rates which are increased by a factor of up to 10^{17} . There have been attempts (12, 25, 28, 31) to remedy this situation, and although there have been claims to have reduced this factor, none of these "corrected" approaches has been widely successful in predicting experimental results. Experiments by Allen and Kassner (8) have indicated that the classical nucleation rate for water vapor is already too large by a factor of $\approx 10^4$. This indicates an overall disagreement of 10^{21} between theory and experiment. Wegener (26) also finds that in the homo-

DISCUSSION OF THE MODEL

The general statistical mechanical theory of condensation is not new (14). These theories have generally assumed that the clusters are composed of molecules interacting weakly through pairwise forces. These forces are assumed to be only a function of the distance between the molecules. Certain molecular configurations, known as irreducible clusters, are predicted and lead to cluster integrals which have only been evaluated for a few specific cases. Accordingly, asymmetric molecules such as water, which interact with one another relatively strongly, have been considered too difficult to tackle theoretically.

We shall assume that the clustering of water molecules occurs through the mechanism of hydrogen bonding. Since the hydrogen bond energy is about 10 times kT for room temperatures, spontaneous changes in the cluster structure between collisions with other gas molecules will be unlikely. We also assume that the relatively tightly bound clusters proposed for our model are capable of supporting normal mode oscillations.

The tetrahedral coordination of hydrogen bonds in water limits the number of possible configurations which a given number of molecules can assume (15). Between successive collisions of the cluster and external molecules, the cluster can be considered to be a complex macromolecule, undergoing innumerable normal mode oscillations. It is assumed that,

following each collision, the cluster will quickly assume the most favorable configuration commensurate with the overall energy state in which the cluster finds itself. It is also assumed that only those configurations corresponding to a given g , for which the frequency of occurrence is reasonably large, need be considered. Since it is impossible to ascertain a priori those cluster structures which provide the lowest energy, models are constructed which closely maintain the preferred tetrahedral angles and bond lengths, maximize the number of bonds, and exhibit the maximum symmetry. Pauling's clathrate cage structure presents a particularly favorable type of model both from the standpoint of energetics (16) and symmetry. An extension of the clathrate model allows considerably more symmetry than the ice-like lattice. While the small clusters do not possess the properties of the bulk liquid, the clathrate structure considered here is favored as a local structure for liquid water.

An examination of clathrate-like cluster models reveals that this type of structure begins to incur considerable strain energy when the number of molecules appreciably exceeds 80. As the number of molecules increases beyond 80, increasing amounts of strain energy bring about more disorder. In the limit the model should approach the structure of the bulk liquid phase. Although some strain energy exists for some of the larger clusters considered in this work, the effect is small so it has been neglected. The

clusters studied in this paper are solid-like except that a unit cell (in the sense the term is used in solid state physics) cannot be defined. The clathrate-like structure possesses the wrong kind of symmetry to allow the structure to grow indefinitely using the same sized cell. However, since every molecule has a definite equilibrium position, disorder of the type which exists in normal liquids does not exist until clusters become very large. The clusters considered in this work are all completely structured.

THE EXPRESSION FOR $\Delta A(g)$ AND
THE CONCENTRATION OF g CLUSTERS.

To write an explicit partition function for a g -sized cluster is a difficult task. However, it can be accomplished on the basis of several assumptions which are mentioned below. Assuming $N(g)$ non-interacting clusters of size g in a volume V at a temperature T , we can write the following partition function,

$$Q = \frac{[Z(g)]^{N(g)}}{N(g)!} \quad [6]$$

Here Q is the canonical partition function of $N(g)$ clusters each of size g and with the same structure, so that the single particle partition function $Z(g)$ is the same for all of the clusters. The Helmholtz free energy of this system, A , is given by the expression

$$A = -kT \ln Q.$$

From the last two equations the expression for the free energy per cluster, $A(g)$, is given by

$$A(g) = A/N(g) = \frac{1}{N(g)} (-kT \ln Q) = -kT \left(\ln \frac{Z(g)}{N(g)} + 1 \right), \quad [7]$$

where Stirling's approximation is used. For a monomer gas

$$A(1) = -kT \left(\ln \frac{Z(1)}{N(1)} + 1 \right).$$

It is customarily assumed that the single cluster partition function, $Z(g)$, can be factored as follows,

$$Z(g) = Z_t(g)Z_r(g)Z_v(g)e^{-E_B/kT}, \quad [8]$$

where $Z_t(g)$, $Z_r(g)$ and $Z_v(g)$ are the translational, rotational and vibrational partition functions respectively. The last factor on the right-hand side of Eq. [8] is a single state partition function representing the contribution due to the total binding energy, E_B , of the system. E_B , which differs from the dissociation energy by the zero point vibrational energy will later be expressed in terms of the hydrogen-bond energy. Here the quantized vibrational states of the system, represented by the partition function $Z_v(g)$, include the zero point vibrational energy. In the same manner since E_B is equal to zero for monomer, the partition function $Z(1)$ is

$$Z(1) = Z_t(1)Z_r(1)Z_v(1). \quad [9]$$

The mean number of clusters of g molecules in equilibrium with monomer gas can be derived from the following particular form of the law of mass action⁽¹⁹⁾

$$N(g) = [N(1)/Z(1)]^g Z(g) \quad [10]$$

or

$$\frac{N(g)}{V} = \frac{N(1)}{V} \exp\{-[kT \ln (Z(g)/V) + gkT \ln (Z(1)/V) - (g-1)kT \ln [N(1)/V]]/kT\}.$$

In analogy with the expression for $C_o(g)$, given by Eq. [5], we define our $\Delta A(g)$ as follows

$$\Delta A(g) = -kT \left(\ln \frac{Z(g)}{V} - g \ln \frac{Z(1)}{V} + (g-1) \ln \frac{N(1)}{V} \right).$$

This $\Delta A(g)$ we call the "free energy of formation". Expressing $N(1)$ in terms of the supersaturation, S , we have

$$\Delta A(g) = -kT \left(\ln \frac{Z(g)}{V} - g \ln \frac{Z(1)}{V} + (g-1) \ln \frac{P_\infty}{kT} + (g-1) \ln S \right).$$

[11]

EVALUATION OF THE PARTITION FUNCTIONS

For a cluster of g water molecules, there are $9g$ degrees of freedom because each molecule consists of three atoms and each atom has three degrees of freedom in a three dimensional space. Of these, six degrees of freedom are associated with rigid-body translation and rotation of the cluster as a whole and the remaining $(9g-6)$ are the internal degrees of freedom. In evaluating Eq. [8] the translational, rotational, and vibrational partition functions will be considered separately.

The rigid-body translation of the whole cluster in a volume V is identical to that of a particle of mass mg moving in the same volume. The translational partition function is therefore given by

$$Z_t(g) = V(2\pi mgkT/h^2)^{3/2}, \quad [12]$$

where m is the mass of a water molecule, k is Boltzmann's constant and h is Planck's constant. Assuming a rigid cluster, the rotational partition function of the cluster is given by

$$Z_r(g) = \pi^{1/2} (8\pi^2 kT/h^2)^{3/2} (I_1 I_2 I_3)^{1/2} \Gamma^{-1}. \quad [13]$$

Here I_1 , I_2 , and I_3 are the principle moments of inertia of the cluster with respect to its center of mass. Γ is the

symmetry number corresponding to the number of physically indistinguishable rotational orientations of the cluster. The moments of inertia are calculated by regarding the monomers as point masses in the cluster.

To find the normal mode vibrations, it is assumed that the cluster can support vibrations about some equilibrium configuration. First, a generalized set of coordinates, representing the displacement of every atom from its equilibrium position, is assigned to the cluster. Next, assuming that the many-body potential energy can be expressed in terms of this generalized set of coordinates, the potential is expanded in a Taylor series about the equilibrium configuration of the system. Since the expansion is around the equilibrium configuration of the cluster, where there is no net force present between the atoms, the first derivative of the potential energy with respect to every member of the generalized set of coordinates is zero. Now assuming a harmonic force field, the third and higher order terms in the expansion are set equal to zero. The quadratic potential energy obtained by this method can, in principle, be written in terms of a special set of coordinates, known as the normal coordinates. The normal modes of vibration can be found by diagonalizing the potential energy matrix. Since such a program is difficult for vapor clusters of large size, we adopt the following method of approximation to get the (9g-6) normal mode frequencies of the system.

The vibrational partition function $Z_V(g)$ of a single cluster is factored into the intramolecular, the libration and the intermolecular vibrations,

$$Z_V(g) = Z_{\text{intra}}(g)Z_{\text{libr}}(g)Z_{\text{inter}}(g). \quad [14]$$

This relation assumes that the coupling between the motion, corresponding to these three different regions of the total spectrum of the cluster, is negligible. In terms of the frequency ν_j (in cm^{-1}), the vibrational partition function $Z_V(g)$ is written as

$$Z_V(g) = \prod_{j=1}^{9g-6} \frac{\exp(-c h \nu_j / 2kT)}{1 - \exp(-c h \nu_j / kT)} \quad [15]$$

where c is the velocity of light. The $(9g-6)$ frequencies correspond to the $3g$ intramolecular, $3g$ librational and $(3g-6)$ intermolecular vibrations, as were separated out in Eq. [14].

This factorization of $Z_V(g)$ is justified in part because of the wide separation in the frequencies associated with the three types of motions. In particular, we note that the $3g$ intramolecular frequencies are much higher in magnitude than the rest of the modes. In other words, the contribution of these modes to the total vibrational spectrum of the cluster is in a distinct region and does not

overlap the rest of the frequencies. In terms of the potential energy of interaction, the obvious assumption has been made that the coupling between intramolecular displacements and the rest of the vibrations in the cluster is negligible. Also it is assumed a priori that the librational spectrum does not overlap either the intra- or intermolecular vibrations. For water, this assumption is justified because only the hydrogens are involved in the hindered rotation of a molecule, so that the ratio of the moments of inertia to the total mass for this molecule is comparatively smaller than the same ratio for other molecular species. In order to deal with these large clusters, spectral data has been used to assign the frequencies for $Z_{\text{intra}}(\text{g})$ and $Z_{\text{libr}}(\text{g})$ while the frequencies for $Z_{\text{inter}}(\text{g})$ were calculated directly.

In deciding on the assignment of frequencies for the intramolecular motions we consider that a free water molecule (vapor) has three modes of vibration. These vibrations consist of two stretching modes and one bending mode, for which the centers of the absorption bands occur at approximately $3,756 \text{ cm}^{-1}$, $3,657 \text{ cm}^{-1}$ and $1,595 \text{ cm}^{-1}$ respectively (17). In the spectrum of bulk water the above three frequencies have the respective values of 3,490, 3,340, and $1,645 \text{ cm}^{-1}$. In order to assign these 3g intramolecular vibrations, the following quantities are defined. Let N be the total number of protons involved in hydrogen bonding and M be the total number of free protons, which are not engaged in hydrogen

bonding in the cluster. Then,

$$N = 2N_4 + 3N_3/2 + N_2 + N_1/2$$

$$M = N_3/2 + N_2 + 3N_1/2$$

where N_4 , N_3 , N_2 and N_1 are the number of molecules in the cluster which are engaged in 4, 3, 2, and 1 bonds respectively. Frequencies at 3,490, 3,340 and 1,645 cm^{-1} , as observed in the spectrum of water, are assigned to the cluster for motion of the protons engaged in hydrogen bonding. Then frequencies at 3,756, 3,657, and 1,595 cm^{-1} , which are the three fundamental modes of a free water molecule, are assigned to protons which do not participate in hydrogen bonding.

In assigning the 3g librational modes, it is noticed that the infra-red spectra of both liquid water and ice have a broad band with a geometric center around 840 cm^{-1} in ice and 630 cm^{-1} in liquid water. Three broad bands with centers at 700, 550 and 450 cm^{-1} have been observed in the librational spectrum of water (21). These frequencies are roughly in proportion to the inverse square root of the three principal moments of inertia of the water molecule (1.02, 1.92, and 2.95×10^{-40} gm-cm^2). Because of this constant ratio, it is possible to assume a constant torsional force constant for assigning librational frequencies to the cluster. Let κ be the twisting force constant of a bond due

to torsion. Also let the average of the libration band for water at 600 cm^{-1} correspond to a molecule participating in four bonds with an average moment of inertia at $1.8 \times 10^{-40} \text{ gm-cm}^2$. A semi-quantitative argument can be constructed to get the approximate librational frequencies for molecules participating in fewer than 4 bonds.

For a 4-bonded molecule, consider libration about an axis parallel to one of the bonds. The total effective force constant of all the bonds is approximately $3\kappa \sin(109^\circ) = 2.8\kappa$. Let α be defined by the relation $\nu = \alpha(K/I)^{1/2}$ where K is in units of κ and I is in 10^{-40} gm-cm^2 . For a molecule participating in 4 bonds, K is 2.8 in units of κ and ν is 600 cm^{-1} ; α is found to be equal to 480 using 1.8 for the average moment of inertia I . Thus, we have

$$\nu = 480 (K/1.8)^{1/2}. \quad [16]$$

This relation is used to find the frequency of the center of the librational band for molecules participating in 1, 2, 3, and 4 bonds.

Special consideration is given to a singly bonded molecule. Here, instead of 3 librational modes about three mutually perpendicular axes, there are one free rotational mode about the bond and two librational modes. These modes will be mixed because of the different possible geometries and will also be broadened by coupling between molecules.

However, since the two librations are about a set of axes perpendicular to the direction of the bond, K is equal to κ , which is equal to 1 in units of κ . From Eq. [16] we get two degenerate libration modes at $480 (1/1.8)^{1/2} = 360$. The lowest band in the bulk water spectrum (centered at 60 cm^{-1}) is assigned to the free rotation of the singly bonded molecule (22).

For a 2-bonded molecule one can show by simple geometry that a threefold degenerate mode at $480 (1.6/1.8)^{1/2} = 450 \text{ cm}^{-1}$ can be assigned to the center of the libration band. Incidentally, this frequency is equal to the Raman active band at 450 cm^{-1} in bulk water. In the same manner one can assign a threefold degenerate frequency at 540 cm^{-1} to the center of the band of a three bonded molecule. Again this is very close to the center of the Raman active band of water at 550 cm^{-1} .

For the intermolecular frequencies, with no further assumptions, the water molecule can be treated as a point mass, and the remaining 3g-6 frequencies found. These vibrations of the cluster are analogous to the hindered translational vibrations which in ice have a frequency range from zero to 300 cm^{-1} . It should be pointed out that thermodynamic functions are most sensitive to low frequencies such as are found in the normal mode spectrum. For this reason a method is developed to set up a so-called secular determinant to calculate these modes.

For the assumption of small vibrations (29) the potential energy for a system of g masses with coordinates Q_1, \dots, Q_{3g} is given by

$$U(Q_1 \dots Q_{3g}) = \frac{1}{2}K_r \sum_{i,j} \delta r_{ij}^2 + \frac{1}{2}K_\theta \sum_{i,j,k} \delta \theta_{j,i,k}^2$$

In obtaining this relation it is assumed, in addition to small displacements of the masses from equilibrium, that the potential energy U depends only on the change in the separation of any pair of molecules (bond stretching, δr_{ij}) and the change in the angle between any three molecules (angle bending $\delta \theta_{jik}$). We further assume that a single force constant K_r , can be associated with all bond stretches and a second force constant, K_θ , with all in-the-plane bends. It is further assumed that all equilibrium bond lengths, l , are equal to 2.8\AA .

In terms of the direction cosines of the bonds, the expression for δr_{ij} is found by expressing the stretching of the bond in terms of the generalized cartesian displacements.

$$\delta r_{ij} = (x_i - x_j)a_{ij} + (y_i - y_j)b_{ij} + (z_i - z_j)c_{ij}$$

Here a , b , c are direction cosines of the bond and x , y , z are the cartesian displacements corresponding to the Q 's.

For $\delta\theta_{jik}$ one can show that

$$\begin{aligned} \delta\theta_{jik} = & \frac{1}{l}[(z_i - z_j)b_{ij} - (y_i - y_j)c_{ij} - (z_i - z_k)b_{ik} + (y_i - y_k)c_{ik}]n_1 \\ & + \frac{1}{l}[(x_i - x_j)c_{ij} - (z_i - z_j)a_{ij} - (x_i - x_k)c_{ik} + (z_i - z_k)a_{ik}]n_2 \\ & + \frac{1}{l}[(y_i - y_j)a_{ij} - (x_i - x_j)b_{ij} - (y_i - y_k)a_{ik} + (x_i - x_k)b_{ik}]n_3, \end{aligned}$$

where n_1 , n_2 , and n_3 , are the direction cosine of the normal to the plane of any three molecules i , j and k . This is the expression for the potential energy matrix, and the kinetic energy T is a diagonal matrix with no cross product terms. The normal modes of vibration are the $3g$ roots of the secular determinant given by the determinantal equation

$$|U - \omega^2 T| = 0$$

where U is the quadratic potential energy matrix, T is the kinetic energy and ω is a frequency. Of all the $3g$ frequencies six of them are zero corresponding to rigid-body translation and rotation of the cluster about its center of mass. Table I lists the 54 normal mode frequencies for the pentagonal clathrate of 20 water molecules (Fig. 3) using a stretching force constant of 1.9×10^4 dyne/cm and a bending force constant of 0.475×10^3 dyne/cm (20). Since this cluster has icosahedral symmetry, only one frequency is nondegenerate and the highest degree of degeneracy is

five. The distribution of frequencies shows that, due to the finite size of the cluster, the low frequencies of less than 40 cm^{-1} and high frequencies of greater than 230 cm^{-1} are absent.

We have now discussed all the terms appearing in Eq. [11], except the evaluation of the monomeric partition function $Z(1)$. This can be calculated by using Eqs. [9], [12], and [13] and the fact that the zero point vibrational energy, including anharmonic terms, of a single water molecule is 13.25 Kcal/mole. The other parameters appearing in Eq. [11], such as temperature, equilibrium vapor pressure and supersaturation ratio, are chosen to correspond roughly to the experimental parameters used by Allen and Kassner (8): $T = 268^\circ\text{K}$, $p = 3.2\text{mmHg}$ and $S = 5.5$.

THE BINDING POTENTIAL ENERGY E_B

In this paper the binding energy of a cluster is defined in terms of the number of hydrogen bonds and the energy associated with each bonding situation. We furthermore assume that the total binding energy can be expressed in terms of two adjustable parameters. Let E_{B4} , E_{B3} , E_{B2} and E_{B1} stand for the energy per hydrogen-bond for molecules engaged in 4, 3, 2, and 1 hydrogen bonds respectively. The total binding energy is written as

$$E_B = 2N_4 E_{B4} + 3N_3 E_{B3}/2 + N_2 E_{B2} + N_1 E_{B1}/2,$$

where N_4 , N_3 , N_2 and N_1 are the number of molecules participating in 4, 3, 2, and 1 bonds respectively. We introduce a cooperative element by supposing that each n -bonded molecule has bonds of the strength (23) given by

$$E_{Bn} = -(1+(n-1)\epsilon)E. \quad [17]$$

Here ϵ and E are two adjustable parameters and n stands for 4, 3, 2, and 1. Substituting the above equation into the previous one, an approximate expression for the total binding energy of a cluster is obtained (in lieu of better information).

$$E_B = -[2N_4 + 3N_3/2 + N_2 + N_1/2 + \epsilon(6N_4 + 3N_3 + N_2)]E \quad [18]$$

The two parameters ϵ and E are adjusted in such a way that the standard deviation of E is a minimum.

An estimate of the value of E and ϵ is in order. Applying Eq. [17] to the case of a singly bonded molecule with $n = 1$ we get an estimate of E , which is the binding energy of a water dimer. This value ranges from -4 to -6.5 Kcal/mole in the literature (24). To get an estimate of ϵ we apply Eq. [17] to a 4-bonded system, namely ice. Since the dipole moment of a 4-bonded molecule in ice is about 40 per cent greater than that of a vapor molecule and about 60 per cent of the hydrogen-bond energy comes from nearest neighbor dipole-dipole interactions, it can be concluded that

$$E_{B4} = -(E + (.6)(.4)E) = -1.24E$$

putting this equal to E_{B4} of Eq. [17], we get an estimate of ϵ at 0.08.

At the present time sufficiently detailed information on the cooperative effect in hydrogen bonding is notably lacking and we have had to make recourse to the classical theory of nucleation to evaluate the parameter E . This is not so much a defect in the theory as a lack of basic information needed for the numerical computations. Recourse to the classical theory does not impair the qualitative conclusions derived from the results.

The exact value of ϵ and E are found through the following procedure. Let ϵ assume values in the range of 0.05 to 0.1. Starting with 0.05, Eqs. [18] and [11] are evaluated for all the cluster sizes in terms of E . By equating these calculations to the corresponding value obtained from the classical expression $\Delta A(g)$, we get a range of values for E . These values are used to find the average value of E and its standard deviation. The procedure is repeated by changing the value of ϵ by 0.001 to get another estimate for the average value of E and its standard deviation. In the above range, we found that $\epsilon = 0.062$ gives the smallest standard deviation for E . The average value of E corresponding to this standard deviation was evaluated at -6.1 Kcal/mole.

NEGLECTED TERMS

In addition to the approximations made, a few important terms have been neglected which will be mentioned briefly here. One is the anharmonic effects corresponding to the third and higher order terms in the expansion of the potential energy. This effect, known only in the case of a single water molecule, changes the zero point vibrational energy from 12.85 to 13.25 Kcal/mole. While this term can be very significant for a large cluster, there is no estimate available of its magnitude. Neglecting this term should not change the qualitative features exhibited in this work. Within the harmonic approximations, the coupling between the intramolecular vibrations has also been neglected. This effect can become very significant because coupling between frequencies of the same type is strong. The same effect obviously exists for the librations where instead of a few sharp bands one broad band actually exists. There is also coupling between intermolecular and the rest of the modes which we have neglected on the ground that the effect is likely to be small.

In addition there are static field effects due to the mutual polarization of the water molecule by its neighbors. This effect causes the dipole moment of a molecule in the cluster to be considerably higher than the value for the free molecule. The strength of the hydrogen bond and the stretching force constant of a bond are affected considerably

by static field effects. We have adjusted the stretching force constant due to this effect to within the ratio of dipole moments in vapor phase to that in ice, i.e. by the ratio 1.3.

RESULTS AND CONCLUSIONS

We have studied clusters ranging in size from 16 to 57 water molecules i.e., clusters of 20, 35, 47, and 57 molecules consisting of one, two, three and four complete interconnected clathrate cages respectively, and some clusters intermediate between these closed cage structures. These intermediate clusters were chosen on the basis of their relatively large number of hydrogen bonds per molecule. Fig. 3 shows pictures of the 20 and 57 cluster models. The larger spheres represent the oxygen atoms and the smaller ones the hydrogens. This picture shows one of many possible orientations of the hydrogens in the cluster. We notice that the angle between the bonds is approximately tetrahedral, that a hydrogen atom is associated with every bond, and that every oxygen atom is associated with two hydrogen atoms so that the water molecule is preserved in the cluster. Since pre-nucleation clusters are not directly observable by any known technique, the assessment of the validity or consistence of the proposed model must depend on its ability to predict the features of measurements which can be made in the laboratory, the nucleation rate being the one of chief interest here.

Fig. 4 is a plot of the isothermal reversible work of formation $\Delta A(g)$ for 15 clusters ranging in size from 16 to 57 molecules. The clusters of 20, 35, 47 and 57 have a free energy of formation considerably less than the value

predicted by the classical theory based on the liquid drop model. The equilibrium concentration of the different size clusters is calculated from Eqs. [5] and [11]. Fig. 5 shows a plot of $C_0(g)$ versus g . Contrary to the liquid drop model, it can be seen that there are many more 20-mers than there are 21-mers or that the concentration of the 57 size cluster is larger than the concentration of the clusters with 56 or 58 molecules. The obvious conclusion is that the closed clathrate structures are considerably more stable. This stability results from the higher binding energy resulting from maximizing the number of bonds. There is also a contribution to the stability of these clusters arising from a shift in the normal mode distribution of frequencies toward higher values.

Fig. 6 shows the distribution of intramolecular frequencies and compares these to those observed in the case of ice. Note that some of the important spectral features of ice are clearly appearing in clusters like the 20 molecule cluster where all the molecules possess only 3 bonds as opposed to the 4 bonds in ice. Burton (30) has made similar calculations for argon clusters at low temperatures.

Note that there is a population increase associated with each minimum in Fig. 4, see Fig. 5. The maxima and minima in the free energy of formation of a cluster of size g provides not one but several barriers to the free

flow of clusters through the cluster distribution when one attempts to calculate nucleation rates. Moreover, the same physical features of these clusters which provide this behavior must be reflected in the evaporation coefficient for a given cluster. This will complicate the kinetic problem and as such will be considered in a later paper.

The possibility of the existence of enhanced populations, such as those exhibited in Fig. 5, offers an alternative explanation of the results of Allen and Kassner (8). As the supersaturation is increased the portions of the curve $\Delta A(g)$ fall faster the larger the value of g . This would mean that the clusters "trapped" in the uppermost stable state can be dumped successively into the nucleation scheme as the supersaturation is increased. Once each "well" of "extra" clusters is depleted the nucleation rate would revert to a lower rate, drawing clusters through the steady-state distribution in much the same way as depicted by the classical theory. Therefore, the "so called" heterogeneous component observed by Allen and Kassner (8) might possibly be explained satisfactorily on the basis of the present work.

In summary, we have assumed a clathrate-like structure for pre-nucleation water clusters and for several of these clusters the free energy of formation has been estimated from a molecular point of view. The results indicate that a molecular model approach to homogeneous nucleation is

feasible. The advantages of such an approach are that 1) it avoids the "translation-rotation paradox" by following a consistent statistical mechanical formulation for the cluster concentration and 2) it does not require the use of bulk properties such as surface tension and surface area for small clusters. It should be emphasized, however, that the results presented here are based on several assumptions including the assumption of small intermolecular vibrations and the separation and the method of assignment of the intramolecular and librational frequencies. In view of the limited information about the hydrogen bond in various environments, these approaches seem reasonable as well as practical. The values used for the hydrogen bond energies have been determined by fitting our $\Delta A(g)$ to the classical free energy of formation, subject to smallest possible standard deviation in parameter E . Thus we cannot propose new numbers for the nucleation rate since this parameterization necessitates agreement with the classical theory. However, the bond energies determined in this way are quite reasonable and are close to the average value per bond in ice. In future work we plan to estimate the binding energies by other methods so that an independent prediction of the nucleation rate can be made. Perhaps the most significant feature of the model is that the $\Delta A(g)$ curve is not the smooth curve predicted by classical theory but shows structure resulting from the internal configuration of the clusters.

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TABLE I
NORMAL MODE VIBRATION FREQUENCIES OF A 20
MOLECULE DODECAHEDRON CLATHRATE STRUCTURE

<u>Degree of Degeneracy</u>	<u>Frequency cm⁻¹</u>	<u>Degree of Degeneracy</u>	<u>Frequency</u>
5	223.4	1	116.6
5	222.9	3	60.8
3	206.8	4	60.3
4	206.3	3	56.7
4	180.6	4	50.8
5	161.5	5	47.1
3	134.6	5	40.7

LIST OF FIGURES

- Fig. 1: Free energy of formation versus the number of molecules g as predicted by classical liquid drop model.
- Fig. 2: Logarithm of the equilibrium concentration of g -mers versus the number of molecules g , as predicted by classical liquid drop model.
- Fig. 3: Cluster models consisting of 20 and 57 water molecules. Large spheres represent oxygen atoms and small spheres represent hydrogen atoms.
- Fig. 4: Free energy of formation as a function of the number of molecules, calculated from Eq. [11].
- Fig. 5: Logarithm of the equilibrium concentration of g -mers calculated from Eqs. [11] and [5] for certain clathrate-like structures ranging in size from 16 to 57 water molecules.
- Fig. 6: The normal mode frequency distributions for clusters containing 57, 53, 47, 43, 35 and 20 water molecules with the optical spectrum of ice.

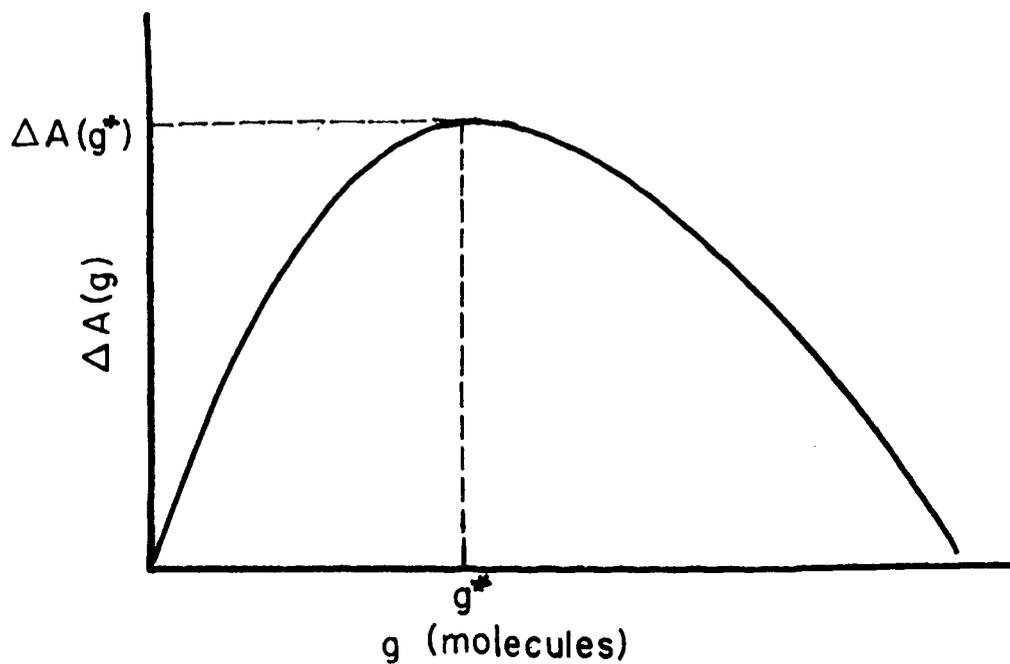


Fig. 1. Behavior of the free energy of formation as predicted by classical theory of nucleation.

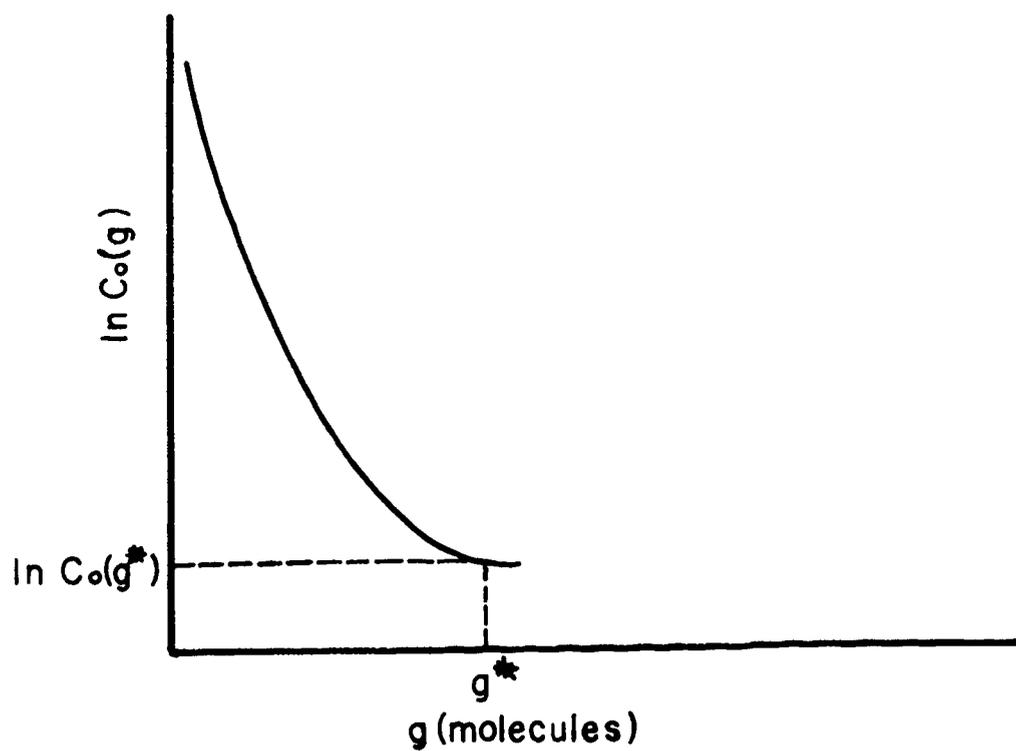


Fig. 2. Behavior of $\ln C_0(g)$ as predicted by classical theory of nucleation.

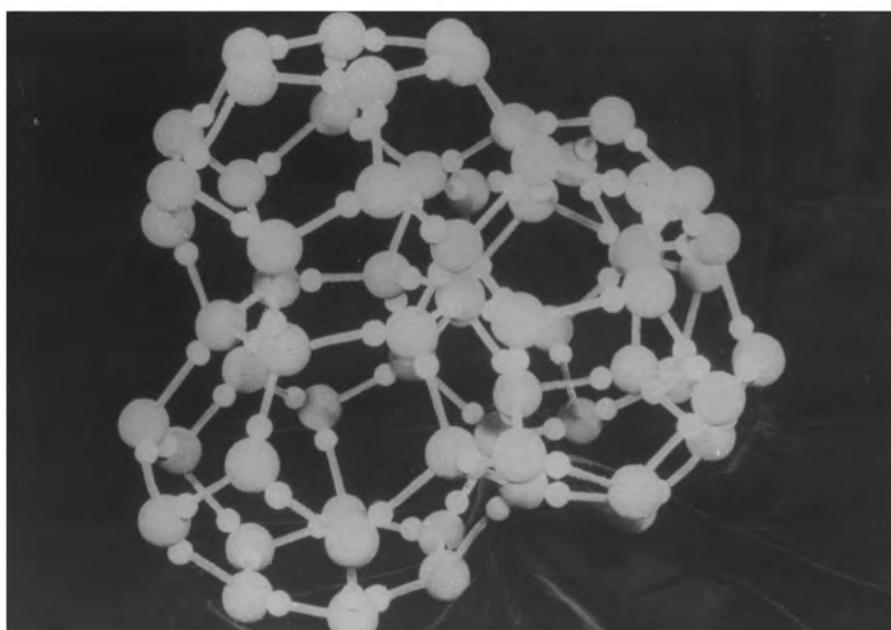
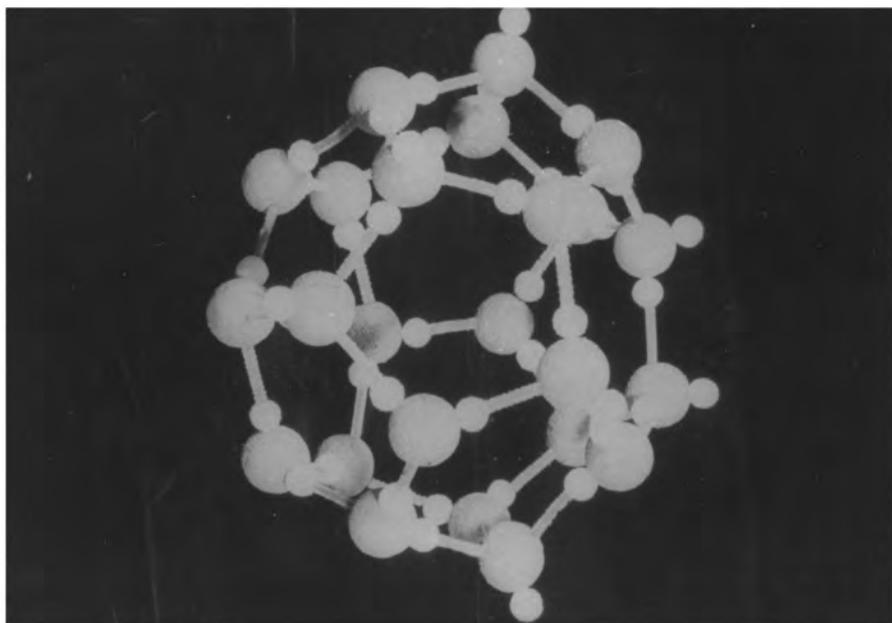


Fig. 3. Clusters Consisting of 20 and 57 Water Molecules.

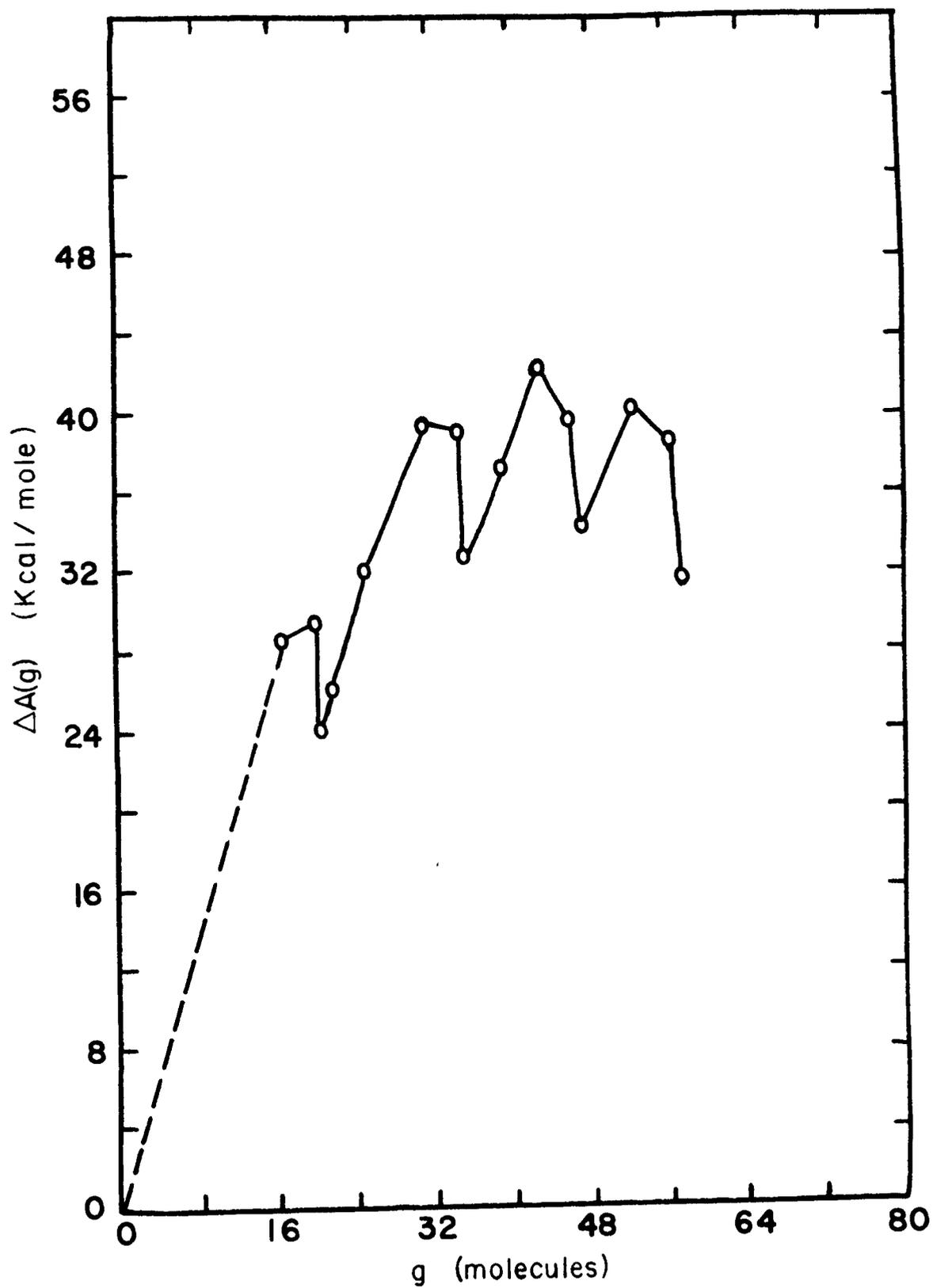


Fig. 4. Free energy of formation as calculated for 15 different clusters ranging in size from 16 to 57 water molecules.

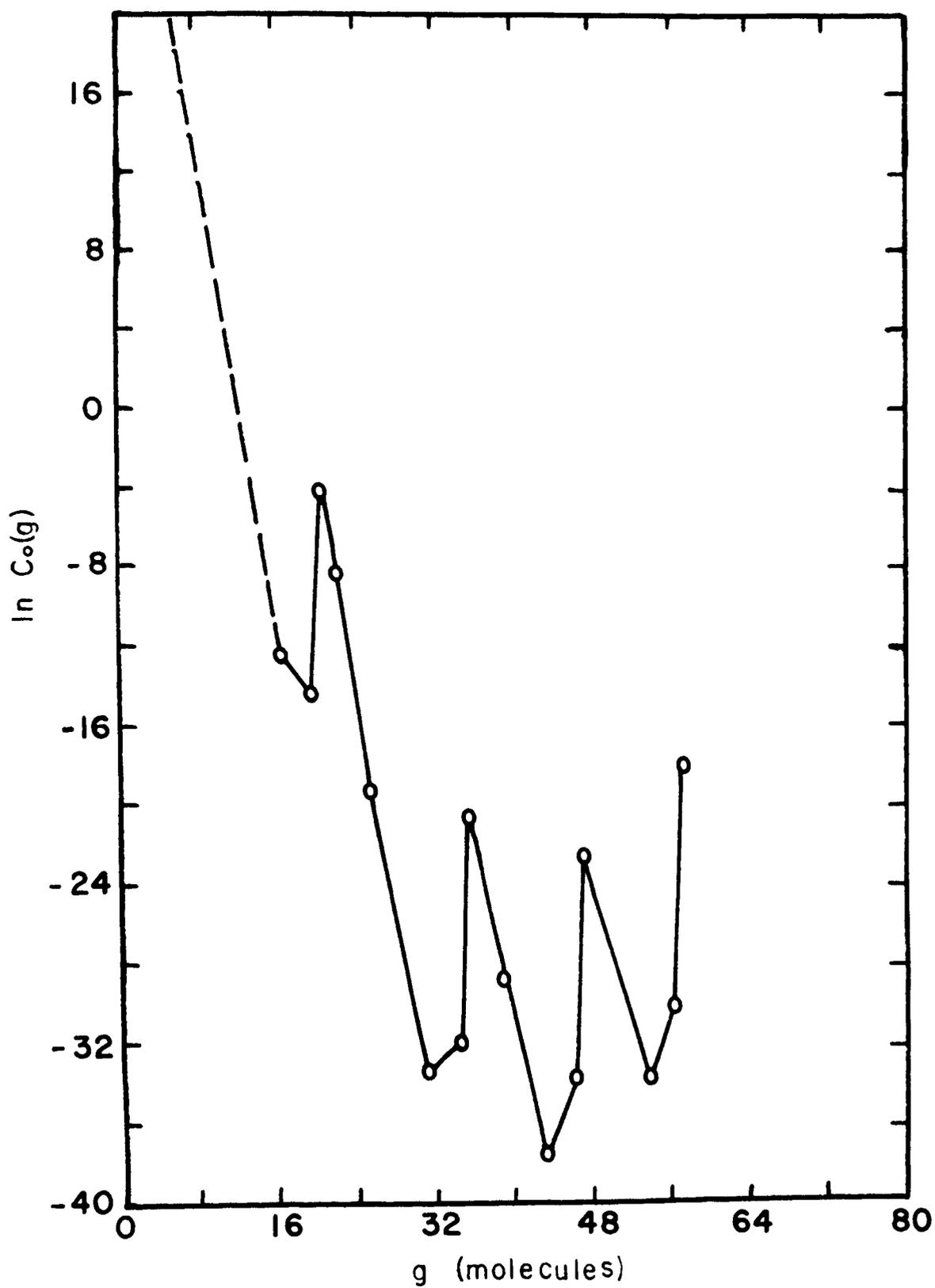


Fig. 5. Plot of $\ln C_0(g)$ for 15 different clusters ranging in size from 16 to 57 water molecules.

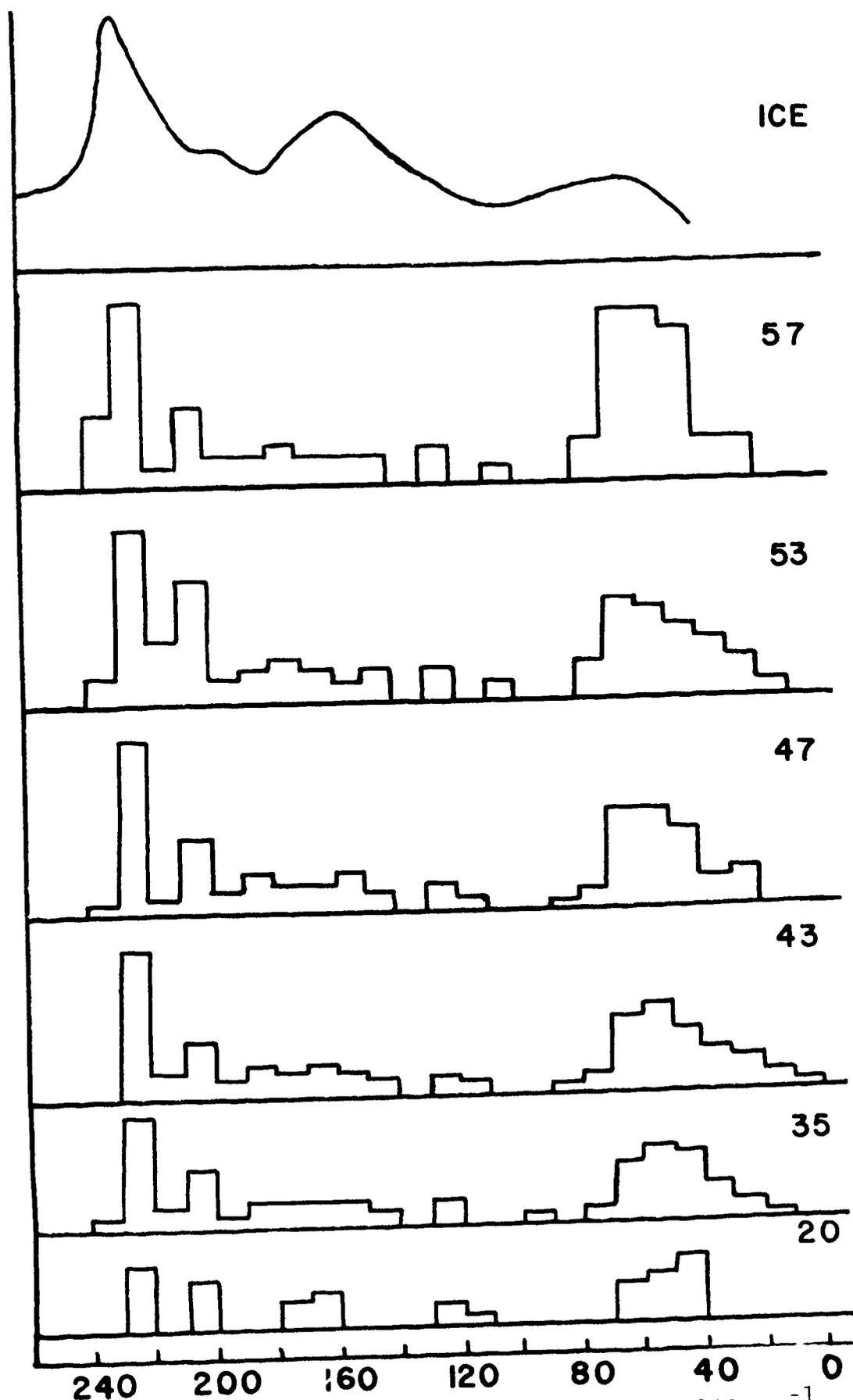


Fig. 6. Frequency distribution in the 0 to 240 cm^{-1} range for 15 different size clusters as compared to ice.

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VITA

Mehdi Daei was born in August 16, 1940 in Dezful, Iran. He graduated from college with a degree in General Engineering in 1963. Upon graduation he went to work for Plan Organization, a planning department, of the Iranian Government.

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APPENDIX

CONTROVERSIES OVER THE WORK OF FORMATION OF A CLUSTER

In this section different models for evaluating the free energy of formation of a cluster are presented. In order not to confuse the issue no account of agreement between theory and experiment is given. The reason being that although there is a total factor of 10^{21} disagreement between theory and experiment, a simple adjustment of the surface tension by about 20 per cent (32) will bring close agreement between theory and experiment. Such an adjustment is not artificial because the theory of surface tension as developed by Kirkwood and Tolman (33) shows, on the basis of quasi-thermodynamic arguments, that the surface tension of a small spherical drop decreases with the radius.

At the present time there is a considerable controversy over the rather subtle points involved in the evaluation of the work of formation of a cluster. The controversy, which is over modifications in the classical "liquid drop" model of nucleation theory, has been presented by a number of investigators in this field. Lothe and Pound suggest that the free energy of a droplet in the capillarity approximation can be computed by summing

up the following contributions: a) the volume free energy of the droplet which is required to condense the supersaturated vapor; b) the surface free energy for creating the droplet surface (this term is estimated as the product of the surface area of the equivalent drop times the surface tension of the bulk liquid); c) the rigid body translation and rotation of the droplet relative to its center of mass; d) correction to free energy of the droplet due to the fact that certain motions which were available to it as part of the bulk liquid are no longer accessible to it as a free stationary droplet in the vapor. This presentation introduces a new factor of 10^{17} in the computed rate of nucleation of water vapor.

Correction d) of the above is known as the replacement factor and before Reiss, Katz, and Cohen presented their version of the subject, the argument was centered on whether or not molecular binding energy is involved in getting an estimate of this correction (11). Present investigation seems to indicate that the replacement factor is purely thermal in nature and corresponds to the deactivation of six degrees of freedom for the motion of the cluster in the bulk liquid assuming that the relative positions of the molecules in the cluster remain unchanged (34,35).

Because of the controversy over the replacement factor, we present Abraham's (36) derivation of the origin of this term. For the sake of simplicity, calculations are made for a linear system of atoms. The stationary (internal) free energy of a finite linear chain of N atoms is expressed as

$$F_i(N) = F_{\text{pot.}} + F_{\text{vib.}} \quad [1]$$

$F_{\text{pot.}}$ and $F_{\text{vib.}}$ refer to the potential and vibrational free energy of the chain respectively. With U_0 being the static energy required to separate two atoms to infinite distance apart, the static or potential part of the free energy for a linear chain of N atoms can be written as

$$F_{\text{pot.}} = -U_0(N-1). \quad [2]$$

The classical expression for $F_{\text{vib.}}$ is the sum of the $(N-1)$ one-dimensional harmonic oscillator free energies corresponding to the $(N-1)$ eigenfrequencies of the system.

$$F_{\text{vib.}} = -kT \sum_i \ln(kT/h\nu_i) \quad [3]$$

where the ν_i 's are the eigenfrequencies of a linear chain of N atoms connected together by $(N-1)$ springs of the same force constant K . It can be shown that

$$\nu_i = (2\pi)^{-1} (4K/m)^{1/2} \sin(\psi_i/2) \quad [4]$$

where

$$\psi_i = (i-1)\pi/N \quad i = 1, 2, \dots, N.$$

Upon substitution of Eq. [4] into Eq. [3] and after some algebraic manipulations, one arrives at the following expression for $F_{\text{vib.}}$:

$$F_{\text{vib.}} = -kT(N \ln(kT/h\nu) - \ln(kTN^{1/2}/h\nu)) \quad [5]$$

where

$$\nu = (2\pi)^{-1} (K/m)^{1/2}.$$

Substitution of Eq. [2] and Eq. [5] into Eq. [1] results in the following expression for $F_i(N)$:

$$F_i(N) = -\{U_0 + kT \ln(kT/h\nu)\}N + U_0 + kT \ln(kTN^{1/2}/h\nu). \quad [6]$$

One notices that the last term is not an extensive function of N .

Now in ordinary thermodynamics, the Euler equation for a chain of N atoms is written as

$$F_i(N) = \mu N + F_{\text{end}} \quad [7]$$

where F_{end} is a constant associated with the free energy of the two free ends of the chain and μ is the chemical potential. Comparison of Eq. [6] with Eq. [7] shows that the last term in Eq. [6] does not correspond to any term in Eq. [7]. The Euler equation, which expresses the thermodynamic potentials as a linear first order function of extensive parameters of the system, is only an exact expression when N is very large, such that $3N-6 \approx 3N$ ($N-1 \approx N$) for a three- (one-) dimensional system. Since Eq. [6] is derived for a finite system, it differs from Eq.

[7]. For this reason the last term in Eq. [6] differentiates the thermodynamic behavior of a small system of finite number of atoms from a large system of ordinary thermodynamics. This term will be referred to as the replacement factor $F_{\text{rep.}}$ and is given by

$$F_{\text{rep.}} = kT \ln(kTN^{1/2}/h\nu). \quad [8]$$

The following results concerning the nature of $F_{\text{rep.}}$ can be arrived at: a) As can be seen from Eq. [5], the origin of the replacement term is in $F_{\text{vib.}}$. This agrees with the argument of Lothe and Pound that the replacement factor is thermal in nature. For this reason and inasmuch as the molecular entropies of many liquids is of the order $5k$, Lothe and Pound estimated (34) the replacement free energy $F_{\text{rep.}} = sT$ at $5kT$. b) To explain this second point, the replacement energy is defined as the difference between the free energy of a finite stationary system of N atoms and the free energy of a mathematical cluster of N atoms which is part of the bulk liquid, except for possession of surface or ends. The N atoms in the bulk liquid go through oscillations which give rise to fluctuations in the position of the center of mass. In contradistinction the center of mass is fixed for the free cluster, so that the center of mass motion of the mathematical cluster should be deactivated in making the transition from the mathematical to the free physical cluster. Since the translational free energy due to motion of the

center of mass of a chain of N particles is proportional to $\ln(N^{1/2})$, he arrives at the conclusion that the replacement factor corresponds to the deactivation of the translational motion of the center of mass of the mathematical cluster in the bulk liquid. Obviously the dependence would be like $\ln(N^{3/2})$ for a system of N particles in three dimensions. In any case, a numerical estimate of Eq. [8] for $N = 100$ is about $3kT$ which is very close to the estimate made by Lothe and Pound. At this point one should make note of the fact that Lothe and Pound were the first to correctly estimate the replacement factor.

More recently Lothe and Pound estimate the replacement energy by deactivating six translational and torsional vibrations of the cluster for which the relative positions of the molecules in the cluster remain unchanged. One notes that the success of the above derivation of the replacement factor is not due to an artificial separation of certain terms. The reason being that the intermolecular potential energy between two particles, has a minimum corresponding to the equilibrium position of the particles. Expansion of the potential energy about this minimum results in the appearance of the static and the thermal potential energies.

Kikuchi (31) rejected the above representation of the replacement factor for the simple reason that the

static and thermal effects should be treated as a unit. For example, in the case of an intermolecular potential, $\Phi(r)$, given by

$$\Phi(r) = U_0 + 1/2K(r-r_0)^2,$$

the partition function can be written as

$$Q = (2\pi mkT/h^2)^{1/2} \int_{-\infty}^{+\infty} \exp\{-\Phi(r)/kT\} dr = (kT/hv) \exp(-U_0/kT).$$

According to Kikuchi the free energy $F = -kT \ln Q$ should be treated as one term, that is

$$F = -kT \ln(\exp(-U_0/kT) (kT/hv)),$$

not as a sum of static and thermal term given by

$$F = U_0 - kT \ln(kT/hv).$$

Since the replacement factor was defined for deactivating the motion of the center of mass of the cluster in the bulk liquid phase assuming that the relative distances between the particles of the cluster remain unchanged, this objection seems to be groundless. Such a motion is thermal only and does not carry with it a static part because the relative positions of the molecules in the cluster were defined to remain constant.

While inclusion of the Lothe and Pound factor changes the calculated rate of nucleation by a factor of 10^{17} , Reiss, Katz and Cohen calculate a much smaller factor of about 10^4 . We follow reference (13) in deriving the expression derived by Reiss and Katz for the free energy

of formation of a cluster. In their presentation Reiss and Katz argue that a snapshot of the supersaturated vapor of N molecules in a volume V and at a temperature T at any instant shows that the N molecules are partitioned among clusters of different sizes. This assembly of various size clusters can be treated as a mixture of ideal gases. The total partition function, Q , can be written

as

$$Q = \prod_i \frac{q_i^{n_i}}{n_i!},$$

where n_i is the number of clusters of size i and q_i is the partition function of an i -molecule cluster given by

$$q_i = \frac{\gamma^i}{i! h^{3i}} \int_V \dots \int_V \exp\{-\beta u_i(r_1, \dots, r_i)\} dr_1 \dots dr_i,$$

where $\beta = 1/kT$ and integration over the momenta has resulted in the γ^i factor. u_i is the potential energy and integration over the volume V is only meaningful over the region where the i molecules are in the force field of each other. In order to make progress, Reiss and Katz introduce a specific model. This model, which Reiss himself rejected in a later paper, defines a spherical volume with its center always on the center of mass of the cluster such that the relative distance between the center of mass and the spherical boundary of the cluster is always fixed. Reiss later (37) notes that such a model is unrealistic because it does not possess the correct

collective properties.

The properties of a droplet can not be assigned to such a cluster because in contrast to this model, the center of mass of a droplet changes with respect to its boundary. Continuing with the derivation of Reiss and Katz, the partition function q_i is written in terms of the center of mass by a linear transformation to center of mass coordinates. Since i^3 is the Jacobian of transformation,

q_i becomes

$$q_i = \{(2\pi mkT/h^2)^{3/2} V\} \left\{ \frac{\gamma^{i-1} i^{3/2}}{i!} \int_{v_i(0)} dr_2 \dots dr_i \exp(-\beta f(r_2 \dots r_i)) \right\},$$

where

$$\gamma = (2\pi mkT/h^2)^{3/2}. \quad [9]$$

Since the last factor (containing integration over the the volume) in Eq. [9] is the configuration partition function relative to the center of mass and the center of mass is temporarily pinned down at the origin in order to evaluate the relative configurational partition function, the volume of integration is expressed as $v_i(0)$.

One can write

$$q_i = \frac{\gamma^i}{i!} \int_V Z(0) dR = \frac{\gamma^i}{i!} VZ(0) \quad [10]$$

where R is the coordinate of the center of mass and $Z(0)$ is the configuration partition function with the center of mass fixed at the origin. If λ_i denotes the partition

function of an i -molecule droplet one can write

$$\lambda_i = \frac{\gamma_i}{i!} \int_{v_i} dR \{ i^3 \int_{v_i(R)} \dots \int \exp(-\beta f(r_2 \dots r_i)) dr_2 \dots dr_i \}. \quad [11]$$

Comparison with Eq. [9] shows that in Eq. [11] the center of mass coordinate R is confined to the volume v_i of the droplet because Reiss is referring to a stationary drop with fluctuating center of mass. Also in Eq. [11] the limit of integration of the relative configuration partition function is changed from $v_i(0)$ to $v_i(R)$ because in a droplet the relative distance between the center of mass and the boundary of the drop is defined to depend on the position of its center of mass.

The last equation can be written as

$$\lambda_i = \frac{\gamma_i}{i!} \int_{v_i} Z(R) dR$$

and q_i can be rewritten by substitution from the last equation into Eq. [10].

$$q_i = \lambda_i V \{ Z(0) / \int_{v_i} Z(R) dR \} = \lambda_i V P(0), \quad [12]$$

where $P(0)$ is the probability of finding the center of mass at the origin. Since λ_i is the partition function of a fixed droplet, it is related to the free energy of a drop $A_i^{(d)}$ by

$$A_i^{(d)} = -kT \ln \lambda_i = i\mu_1 + \alpha i^{2/3}. \quad [13]$$

The last two terms are proportional to the bulk and sur-

face free energies of the droplet respectively. Because in the classical liquid drop model the free energy of a cluster is assumed to be that of a droplet given by Eq. [13], the extra factor of $VP(0)$ in Eq. [12] is a new correction to the classical model. Reiss and Katz, using a Gaussian distribution for representing $P(R)$, estimated that this correction increases the classical rate of nucleation by a factor of 10^4 . This factor is much smaller than the 10^{17} factor predicted by Lothe and Pound.

The essence of the above discussion can be summarized noting that the cluster partition function q_i , was written as

$$q_i = q_{tr.} q_{int.}$$

where $q_{tr.}$ and $q_{int.}$ are the translational and internal partition functions respectively. The internal partition function includes rotational motions. Furthermore, $q_{tr.}$ is given by

$$q_{tr.} = i^{3/2} \gamma V. \quad [14]$$

For the stationary liquid drop (stationary in the sense that its boundaries are fixed but its center of mass moves around) the translational partition function $q_{tr.}^{(d)}$ can be written as

$$q_{tr.}^{(d)} = i^{3/2} \gamma / P(0). \quad [15]$$

The equilibrium number of i -molecule cluster can be expressed in terms of q_i and the chemical potential of the vapor μ_1 by the following relation (13):

$$n_i = q_i \exp(i\mu_1/kT) = q_{tr.} q_{int.} \exp(i\mu_1/kT), \quad [16]$$

where partition function of the drop, $q_i^{(d)}$, (same as λ_i) is given by

$$\lambda_i = q_i^{(d)} = q_{tr.}^{(d)} q_{int.} = \exp(-i\mu_1\beta - \beta\alpha i^{2/3}). \quad [17]$$

One can substitute for $q_{int.}$ from Eq. [17] into Eq. [16] to get

$$n_i = (q_{tr.}/q_{tr.}^{(d)}) \exp\{-\beta i(\mu_L - \mu_1) - \beta\alpha i^{2/3}\} \quad [18]$$

The factor in the exponent is the work of formation, $W(i)$, so that

$$n_i = q_{tr.}/q_{tr.}^{(d)} \exp\{-W(i)\beta\}. \quad [19]$$

The extra factor of $q_{tr.}/q_{tr.}^{(d)}$ can be interpreted to be due to the translation of the cluster throughout the volume V except for those regions which correspond to the motion of the center of mass of the drop. The division by $q_{tr.}^{(d)}$ subtracts out these regions because they have already been accounted for in the work of formation $W(i)$.

To reconcile the two approaches of Lothe and Pound on the one hand and Reiss and Katz on the other, one notices that the final result of Reiss and Katz, as expressed by Eq. [19], corresponds to the following final relation derived by Lothe and Pound:

$$n_i = q_{tr.} q_{rot.}/q_{tr.}^{(d)} q_{rot.}^{(d)} \{\exp[W(i)/kT]\}. \quad [20]$$

Here the assumption is made that the stationary drop differs from an equivalent spherical region of the bulk liquid only by the possession of surface. On the basis of

this assumption $q_{tr}^{(d)}$ is meant to be the same in both Eqs. [19] and [20]. The only difference between these two equations would be the appearance of the rotational partition functions in Eq. [20] which Reiss and Katz did not factor out in arriving at Eq. [19].

This point of view seems to be correct because: a) According to Kikuchi (31) the configurational partition function of a homogeneous system of molecules is the product of the molecular volume times the relative (fixed point) partition function. Any further factorization of a partition function does not seem to be consistent with the non-rigid cluster model of Reiss and Katz; b) The spectra of the polyatomic molecules show small contributions from rotational motion for large molecules. Such experimental data favors neglecting rotational effects for a cluster of 100 molecules; c) Abraham (19) suggests two extreme models to estimate the rotational partition function. The first model being the restricted cell model with zero communal entropy (quasi-crystalline liquid drop) and the second being the unrestricted cell model in which the molecules of the cluster wander over the entire volume of the cluster. For this reason the possible range of values for the rotational partition function of the cluster corresponding to the above two models vary from 10^9 in the first case to unity for the second model.

As was mentioned, Reiss in a recent paper (37) has rejected the Reiss and Katz model on the ground that the collective properties of such a cluster does not correspond to a stationary drop. He proposes a new model based on the natural requirement of the phenomena, namely that such a model should have collective properties of fixed boundaries but fluctuating center of mass. The properties of "liquid drop" is associated with this model which Reiss refers to as drop-like model.

In order to satisfy the requirement of a stationary boundary as in a droplet, Reiss confines the *i*-molecule cluster inside a Gibbs dividing surface. Now the molecules of the cluster can move around inside this sharp surface and as a result the center of mass of this droplet like cluster fluctuates like a liquid drop. For a system of 100 molecules the mass density varies as a function of the radius of the drop in going through a transition region where it adjusts from the liquid like density at the center of the cluster to the vapor like density at the outside. For this reason it is necessary to choose a mathematical Gibbs dividing surface (surface of tension) in order to define the boundaries of the cluster. On the other hand the physical cluster radius can not be very large for this is unfavorable energetically. It also

can not be too small because this is not favorable from an entropy point of view. For this reason Reiss assumes a unique radius for the n_i cluster of size i . Accordingly, any deviation from this size is not favorable and the probability of its existence is practically zero. Next, Reiss assumes a unique dependence between the radius r and the number of molecules, given by $r(i)$, and determined by the outside temperature and pressure. Based on the above representation and because of the lack of information on the density as a function of radius the only way to proceed is to define a mathematical surface of tension such that it coincides with the physical, i.e. the most probable, radius of the cluster. For the critical size cluster which is in equilibrium with the outside vapor, this mathematical surface should be chosen such that the vapor pressure p_i of the cluster is equal to the outside pressure. Such a surface should be defined at a radius where the density of the drop-like cluster has reached that of the outside vapor. For the pre-nucleation clusters which are not in equilibrium with the outside vapor, Reiss argues that since a cluster is relatively isolated at all stages of its development, it can be treated as the critical cluster for the purpose of defining a surface of tension for it. More precisely since the outside pressure can only influence the rate

of cluster formation, one can define the same radius $r(i)$ whether the cluster is or is not in equilibrium with the surrounding vapor.

The drop-like cluster defined above is released so that it translates over the whole volume of the system to generate all possible configurations, which leads to the evaluation of the configuration integral. The work of formation, $w(i)$, evaluated by the above method or by a computation of the reversible work effects is found to be

$$w(i) = W(i) - kT \ln(p_i/p), \quad [21]$$

where $W(i)$ is the classical work of formation of a "liquid drop". Assuming $p_i = p$, then $w(i) = W(i)$ and there is no replacement energy.

The above result can be derived by the following simple reasoning. The drop-like cluster proposed by Reiss can be compressed isothermally to an equivalent size liquid drop containing the same number of molecules. During this compression the surface of tension moves to a smaller size and the dense vapor which is smeared around the outside boundary of the cluster changes into liquid. In the case of the critical size cluster where $p_i = p$, the free energy of formation does not change during this phase transition. As a result we have changed the drop-like

cluster into a liquid drop with no extra work and for this reason the replacement factor is unity. The application of this argument to a pre-nucleating cluster at pressure p_i is obvious. In this case the work done for this compression is $-kT \ln(p_i/p)$ which is the replacement term predicted by Reiss.

The above discussion takes us back to the starting point of defining a cluster. From the thermodynamic point of view such a definition is arbitrary. In the case of the physical clusters in nucleation theory, all the physically reasonable definitions should lead to rather similar values for the equilibrium concentration of different size clusters. In general, the stronger the internal forces in between the molecules of a cluster, the greater tendency for different definitions of a cluster to converge to the same predictions. Such is the case for clustering of water molecules. The strong forces between water molecules, should lead to a unique prediction for the equilibrium concentrations. This in turn should result in a unique prediction of the rate of nucleation.