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Structural strain in small prenucleation water clusters

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A method is developed for incorporating strain energy into a microphysical treatment of small prenucleation water clusters. The molecules are arranged in a clathrate-cage structure, and this structure is allowed to relax to minimize the strain energy resulting from hydrogen bond stretching and bending. The method is applied to various cluster sizes up to 130 molecules and the results are compared with the classical liquid drop model. The effect of anharmonic terms in the interaction is included.

I. INTRODUCTION

In order for man to progress in understanding and modifying weather processes, he must first build a firm foundation in the fundamental chemical physics of ice and water. Many of the important atmospheric processes involve particles in the very small size range and cannot be successfully addressed by the classical macroscopic theories. Of particular interest is the vapor to liquid and the supercooled liquid to ice transition and their release of the vast amounts of energy associated with the phase transitions of water.

In nucleation theory the traditional method for treating small liquid droplets has been to treat the material as a continuum and extrapolate bulk properties such as surface tension and density down into the region of these very small prenucleation clusters.[1] Such an approach was found to yield good results for homogeneous nucleation rate measurements for water at slightly above the critical supersaturation.[2,3] However, the classical theory has a conceptual weakness in that it does not account for the energy of translation and rotation of the droplet's center of mass. When this energy is included in a hybrid classical-statistical mechanical theory,[3] the quantitative agreement with nucleation rate experiments is lost.[4] Another weakness develops when the theory is extended to smaller cluster sizes. As the number of molecules in the cluster goes down, the fundamental continuum approximation must eventually break down and give way to effects resulting from the discrete molecular nature of the cluster.

In order to surmount these difficulties the general problem of nucleation has been approached by several techniques on a molecular level. Ben-Naim and Stillinger[5] have developed an effective pair potential for the water–water interaction. Using the interaction potential Rahman and Stillinger[6] developed a molecular dynamics model which has proven successful for the description of bulk liquid water, and in principle it could be extended to give information concerning vapor to liquid nucleation. It is impractical, however, to directly apply this molecular dynamics technique to water in the vapor phase. Because of the much lower density in the gas phase, the number of molecules and hence the number of variables treated in the model would have to be increased far above that used in the bulk water problem in order to make condensation a realistic possibility. Furthermore, the system would have to be allowed to evolve for a substantial length of time before spontaneous nucleation

would occur. This would make the computer time impractically long. Other models for liquid water are reviewed by Eisenberg and Kauzmann,[7] but were not deemed suitable for the nucleation problem.

The statistical mechanical theory of nucleation of spherically symmetric weakly interacting molecules has been developed by several workers, e. g., Band,[8] Reiss,[9] and Abraham,[10] but the method results in cluster integrals which have not been very successfully evaluated for water. This type of treatment probably overestimates the contribution due to permutation and disorder phenomena. It does not account for the structure and detailed intermolecular interactions within the nucleation cluster. Since the hydrogen bond is about $10kT$ at room temperature this intermolecular structure is an important facet of the problem for water. Burton,[11] McGinty,[12] and Abraham and Dave[13] have developed statistical mechanical treatments for the nucleation of argon clusters which do account for the internal structure of the cluster. Spherically symmetric Lennard-Jones potentials are used to describe the intermolecular interactions. This model has yielded interesting results for such systems but was not applied to the case of water because of the complex nature of the internal structure of the water molecule and of its intermolecular interactions.[14,15] Also, it would not be practical to apply this method to larger clusters. Strain does not arise in this model because of the spherical symmetry in the intermolecular potentials.

During the past five to ten years a very successful molecular model for water clusters has evolved in this center which has shown the good agreement with experiment which was once held by the uncorrected classical liquid drop model. In this model the water molecules are arranged in a definite microcrystalline structure, held together by elastic hydrogen bonds. Different structures are modeled in order to find the lowest "free energy of formation" for a cluster containing a given number of molecules. The most favorable structure is found to take the general form of the dodecahedral clathrate cages first suggested by Pauling.[16] The cages have 12 faces, each made up of a five-membered ring, and they retain the high degree of tetrahedral symmetry preferred by the electronic structure of the water molecule. In order to construct a statistical mechanical theory for microcrystalline clusters of water molecules, a generalized method for calculating the intermolecular vibration spectrum of the clusters had to be devised. Bolander

et al.[17] conceived of utilizing a classical mechanical approach but failed to devise a generalized normal coordinate system. The latter was devised by Daee et al.[15] and Plummer.[19] Plummer and Hale[20] have done extensive work in developing and refining the model. Using the clathrate structure an approximate canonical partition function is evaluated under the assumption that it can be factored into separate terms for intermolecular, intramolecular, and librational modes. This partition function then yields the thermodynamic properties of a representative number of water clusters.

One property of the clathrate structure is that it cannot be used as a basic building block for an infinite periodic array of molecules. Hence, the ordered structure used in the molecular model cannot be extended indefinitely in size without encountering excessive amounts of strain energy. It was found that clusters larger than 60 or 80 molecules could not be built without grossly distorting the hydrogen bond lengths and bond angles. Distortions generate strain energy which should be accounted for in the free energy of formation during the statistical mechanical analysis when these larger clusters are treated. Furthermore, the molecular model probably underestimates the effect of permutations and disorder phenomena. The incorporation of structural strain is an attempt to account for one facet of the disorder in a realistic manner in strongly bonded systems. In this paper we shall endeavor to treat this problem of strain energy in large clusters of water molecules. Problems dealing with the transition layer at the surface of ice will be dealt with in subsequent papers.

The behavior of water clusters and their associated strain in the size range larger than 60–80 molecules is of definite interest. One test of the validity of the microscopic model would be to show that its predictions merge with those of the classical liquid drop model when the cluster size becomes sufficiently large so that the continuum approximation is valid. For the size 57 cluster[19] the intermolecular vibration frequency spectrum fades out above 240 cm^{-1}. However, the infrared spectrum of ice shows some vibrational modes near 300 cm^{-1}, which appear to be intermolecular in nature. There is a need to study the spectrum of larger clusters to see if these 300 cm^{-1} modes can be identified. At some point in between the very small clusters which exhibit the clathrate type structure and perfect tetrahedral symmetry and the very large clusters which behave as a continuum, the clusters will have to deviate from their perfect order because of strain. Cracks will appear to relieve the strain, even at the expense of a few hydrogen bonds. Bond breaking and making in the vicinity of such cracks would give these features a highly dynamic character resembling the disorder phenomena of bulk liquid water as seen in Rahman and Stillinger's molecular dynamics treatment of liquid water.[6] Another possibility would be the appearance of some six-membered rings to replace a few of the usual five-membered rings. The ability to treat strain is a prerequisite to studying the structural characteristics. Another motivation for looking at larger clusters lies in the fact that the critical cluster size involved in the homogeneous nucleation rate

depends on supersaturation. For low supersaturation and low temperature the critical cluster size will be well into the size range where strain is significant. Even some cases of quasiheterogeneous nucleation, such as nucleation on ions at low supersaturations,[21] can involve large critical cluster sizes. Other important problems appropriate for the molecular theory deal with the equilibrium distributions of clusters on surfaces[22] and the capture of foreign molecules into the cavities of the clathrate cages.[23] Preliminary work in this area by Biermann[23] suggests that cluster strain is an important parameter. Hence, the following method for treating strain has a wide variety of applications in molecular dynamics problems.

II. STRAIN CALCULATION METHOD

Strain energy is defined as arising whenever a hydrogen bond is stretched or the bond angle is bent and the resulting bond energy is less than the energy of the bond under the most favorable configuration. In our model we limit ourselves to the intermolecular aspects of the strain by treating the molecules as points. The energy required to deform the molecule itself is much larger than that required for intermolecular deformations and hence can be neglected. Initially we use harmonic approximations for the intermolecular forces. In this approximation the strain energy generated by a stretched bond is given by $\frac{1}{2}k_r(r-r_0)^2$, where $k_r = 0.19 \times 10^5$ dyn/cm is the bond stretching force constant, r is the length of the stretched bond, and r_0 is the equilibrium separation which is taken to be 2.76 Å. The strain energy generated by a deformed angle is given by $\frac{1}{2}k_\theta(\theta-\theta_0)^2$ where k_θ = 5.19 kcal/mole is the bond angle bending force constant, θ is the bond angle, and θ_0 is the equilibrium value of the bond angle. k_r and k_θ are approximately the force constants for ice.[7] θ_0 is taken to be 108° so that there is no strain in the basic five-membered ring. In order to calculate the strain energy in a given cluster one determines the distortion in each bond length and angle, calculates the corresponding strain energy contribution, and then sums all of these terms. The resulting total strain

$$E_s = \frac{1}{2}k_r\sum_{ij} (r_{ij}-r_0)^2 + \frac{1}{2}k_\theta\sum_{ijk} (\theta_{ijk}-\theta_0)^2 \tag{1}$$

is thus a function of the coordinates of all the molecules in the cluster.

Our technique for determining the structure and the strain energy for a cluster containing g molecules is the following. We first need the approximate Cartesian coordinates for each of the molecules in the cluster. These can be estimated with the aid of ball and stick cluster models. The molecules are first assembled into an approximate structure built up using clathrate cages as the basic building block. We attempt to maintain approximately tetrahedral angles between bonds and maintain bond lengths of approximately 2.76 Å. Only systems containing an integral number of cages were considered at the outset. The five-membered rings making up the cages are not required to close completely. The structure can be quite rough; we only require that the nearest neighbors for each molecule be identified. The
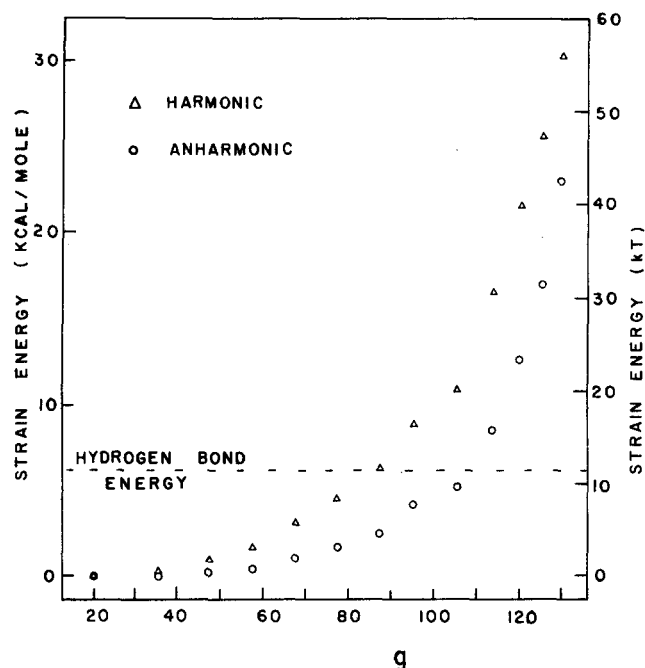
FIG. 1. Strain energy vs the number of molecules (g) in the cluster. Results are shown for both an harmonic and an anharmonic bond bending potential. Energy is shown in units of kilocalories/mole and kT, for $T = 273$ °K.

strain energy for this structure can be calculated from Eq. (1). Since the structure is only approximate, the strain energy will be quite large. We now want to make adjustments in the structure so as to allow the strain to relax to a minimum value. This can be done numerically. We have one nonlinear function of many variables which we want to minimize; the function being the total strain energy Eq. (1), the variables being the Cartesian coordinates of the molecules. Since the strain energy is independent of translation of the center of mass and rotation of the entire system around the center of mass, the actual number of adjustable coordinates is $3g - 6$. For this reason six of the Cartesian coordinates are held constant: the x, y, and z coordinate of molecule 1,

the y and z coordinate of molecule 2, and the z coordinate of molecule 3.

Several computer routines exist for the purpose of minimizing one function of many variables. We obtained the best results with the routine STEPIT.[24] This routine is found to converge quickly in spite of the large number of adjustable variables and it does not require the derivatives of the subject function to be supplied. This numerical process will allow the strain to relax but it will not cause any major structural change on its own, such as the conversion of a five-membered ring to a six-membered ring. Such changes must be put in by hand into the initial approximate structure.

III. RESULTS

This technique has been applied to clusters of various size, and the results are shown in Fig. 1 and listed in Table I. Here we have plotted strain energy vs the number of molecules in the system. Only the results for clusters with closed cages are shown. The first point is for a cluster consisting of one clathrate cage, the second point is for two cages, etc. The last point represents a cluster made up of 13 cages, one cage at the center surrounded by 12 other cages, one covering each of the 12 faces of the central cage. The first few clusters exhibit an insignificant amount of strain since their strain energy is much less than the energy of a hydrogen bond, 6 kcal/mole. In the 60–80 molecule size region the strain begins to become significant in comparison to the bond energy. For larger clusters the strain energy exceeds the hydrogen bond energy and rises rapidly with size. The largest cluster treated, 130 molecules, has about 30 kcal/mole strain energy, approximately the energy needed to break five hydrogen bonds. Hence, for clusters larger than 60 or so molecules, the strain energy is significant and should be accounted for in any microscopic treatment.

The distribution of strain energy for the various cluster sizes is given in Table I. g_s is the number of molecules on the cluster surface. Δr gives the standard de-

TABLE I. Strain energy and its distribution for the various cluster sizes. g denotes the number of molecules in the cluster, g_s the number of molecules on the surface, E_s the total strain energy, Δ_r and $\Delta\theta$ denote the standard deviations in bond length and bond angle, respectively, Δr_{max} and $\Delta\theta_{max}$ give the maximum values for deviations in bond length and bond angle.

g	No. cages	g_s	E_s (kcal/mole)	Δr (Å)	Δr_{max} (Å)	$\Delta\theta$ (deg)	$\Delta\theta_{max}$ (deg)
20	1	20	0.03	0.002	0.008	0.7	2
35	2	35	0.32	0.006	0.021	1.7	9
47	3	47	1.01	0.011	0.043	2.5	11
57	4	56	1.78	0.013	0.040	3.0	11
67	5	65	3.17	0.017	0.075	3.6	14
77	6	74	4.57	0.020	0.069	4.0	14
87	7	83	6.23	0.022	0.073	4.2	16
95	8	89	8.91	0.026	0.088	4.8	17
105	9	98	10.96	0.028	0.095	5.0	20
114	10	107	16.48	0.033	0.089	5.8	22
120	11	110	21.60	0.038	0.105	6.4	24
125	12	110	25.58	0.041	0.113	6.8	26
130	13	110	30.29	0.044	0.113	7.1	27

viation in bond length averaged over all the bonds in the cluster. Δr_{max} is the maximum bond length distortion. $\Delta\theta$ gives the standard deviation in bond angle, and $\Delta\theta_{max}$ is the maximum bond angle distortion. We find that in the central region of the cluster the strain takes the form of a compression, i.e., all of the central bond lengths are shortened. On the other hand, we find a stretching effect on the surface. The maximum bond bending is found to occur on the surface at the points where distinct cages meet. Here we find bond angles which are not interior to any cage, and these angles are required to open up considerably beyond the equilibrium value in order to close all of the five-membered rings which juncture at that molecular site. Strain due to bond length distortion accounts for only a small percentage of the total strain energy with the major part coming from bond bending. Hence, the strain energy would be substantially higher and more evenly distributed between the stretch and bend components, if the potential for bond bending were stronger. In the 20 molecule cluster, bond stretching accounts for only 9% of the total. This percentage increases with cluster size and reaches 20% for the 130 molecule cluster. The major part of the total strain energy is found to be located on the cluster surface. This is a reasonable result since the largest bond bending occurs at the surface and since most cluster molecules lie on the surface anyway, even for the 130 molecule system.

Let us now examine the contribution which the strain energy makes toward the total free energy of cluster formation. The free energy in the classical liquid drop model is given by[1]

$$\Delta\Phi(g)/kT = 4\pi r_g^2 \sigma/kT - g \ln S,$$

where g denotes the number of molecules in the cluster, k is Boltzmann's constant, T is the temperature, r_g is the cluster radius, σ is the surface tension, and S is the supersaturation. The free energy given by the molecular model is[20]

$$\Delta\Phi(g)/kT = [F_{TR}(g) + F_{vib}(g) + (E_B + E_S)/kT]$$
$$- g[F_{TR}(1) + F_{vib}(1) + \ln S],$$

where F_{TR} denotes the free energy contribution from translation and rotation, F_{vib} is the contribution from vibratory motions, $E_B(< 0)$ is the binding energy due to hydrogen bonding, and $E_S(> 0)$ is the strain energy. Figure 2 shows a plot of the free energy vs g as given by the classical liquid drop model and by the molecular model using some recent results.[22,25] The molecular model result is shown both with and without the strain energy contribution. Results for two supersaturations, $S = 1$ and $S = 5$, are shown. The curves for the molecular model are seen to take an unphysical downturn for the larger cluster sizes when the strain term in not included. This is because the binding energy is substantially overestimated when bond weakening due to strain is not included. When the strain term is included in the calculation, the anomalous kink is removed and the curve is shifted noticeably upward for large clusters. The strain does not make a significant contribution below about $g = 47$.
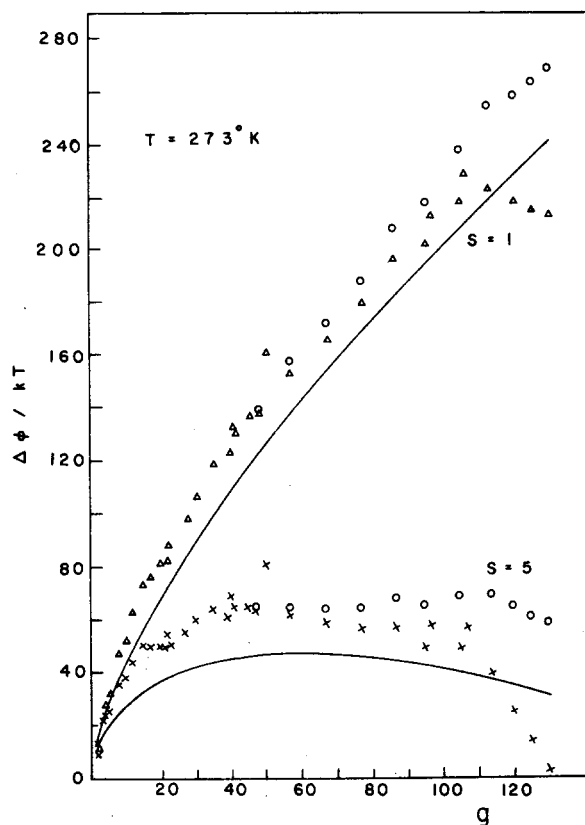

FIG. 2. Total free energy of formation vs number of molecules (g) in the cluster for two supersaturations, $S = 1$ and $S = 5$, and for one temperature, 273 °K. The solid line gives the classical liquid drop model results without any correction factors. $\Delta(S = 1)$ and $\times(S = 5)$ give the results for the molecular model when strain is not included; ○ give the results of the molecular model when it is corrected for strain.

The fact that the strain energy is substantial and that the corrected molecular model does not yet merge with the results of the liquid drop model, as it must eventually do, suggest that some alternate structure must become more favorable energetically than the rather perfect and symmetrical clathrate structure employed in these calculations when the cluster size gets large. To pursue this possibility, we have examined some changes in configuration for the $g = 130$ cluster at a temperature of 277 °K. The total free energy has been evaluated for the lowest energy configuration of the $g = 129$ cluster and for various configurations of the $g = 130$ cluster, first without and then with strain being included in the calculation. All of these energy levels are zeroed against the $g = 129$ level. The results are shown in an energy level diagram in Fig. 3. In the first column we show only one level, that being the one of the lowest energy configuration of the $g = 129$ cluster. The second column contains a series of levels for the $g = 130$ cluster when strain is not included. The lowest level is for our standard structure made up of clathrate cages with all rings closed. The configuration is changed for the next level by breaking one hydrogen bond. The break is made in a bond that lies on the surface at the point where two cages meet and hence is the location of maximum bond bending. The configuration for the next level is changed by breaking two bonds, the same one as before plus the
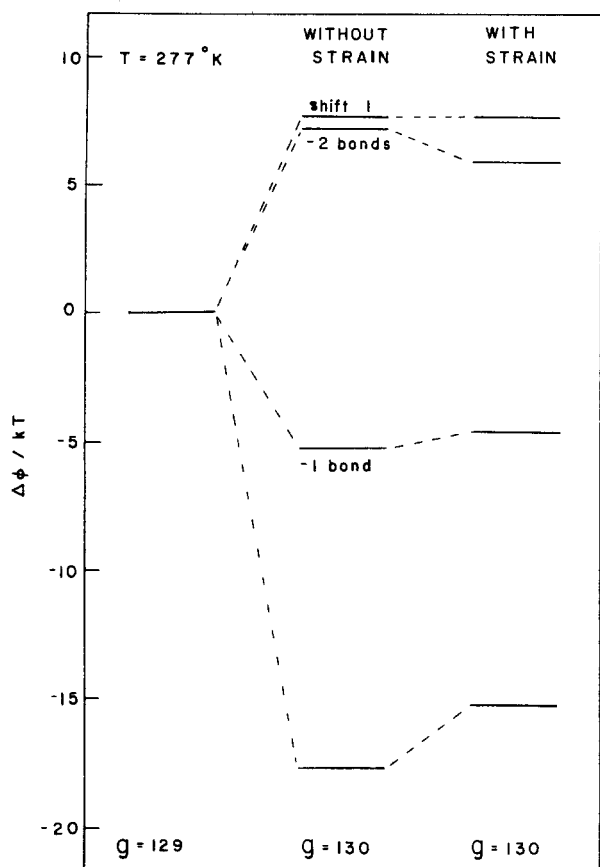
FIG. 3. Energy level diagram showing total free energies for
the 129-molecule cluster and for various configurations of the
130-molecule cluster. Results are shown for the cases where
strain is not included and then again when strain is included.

IV. ANHARMONIC POTENTIAL EFFECTS

Investigation of the large clusters shows that the major contribution to the strain energy comes from bond angle bending and that quite large angular deformations, up to 27°, are involved. These facts suggest the need for a hard look at the harmonic bond bending potential to see if its use could be introducing significant error. Are we pushing the harmonic approximation beyond its range of validity? We do not consider anharmonic effects for bond stretching because it makes such a small contribution to the strain energy.

The problem of intermolecular water potentials, especially for bond bending and for anharmonic terms, has not been explored very thoroughly. The force constants used here have been derived from fits to experimental data.[7] The range of distortions for which these force constants are valid is not known. Theoretical studies of intermolecular water potentials indicate that the bond bending potential may be quite flat near zero distortion because the line of proton-donor approach can be easily bent away from the lone-pair-favored direction.[14] It is quite likely that the potential is weaker than harmonic for small angles and stronger than harmonic for larger angles. However, the task of generating a good bond bending potential model from theoretical quantum mechanical calculations is made quite difficult by the existence of known cooperative effects in hydrogen bonding which lead to nonadditivity of hydrogen bond energies.[15] A potential which is valid for a trimer may not be valid

corresponding bond in the neighboring surface cage. The configuration for the top level is altered by removing one of the triply bonded surface molecules, shifting it over to the other side of the cluster, and reattaching it to another triply bonded surface molecule. It now looks like a monomer that is single bonded to a $g = 129$ cluster.

When the strain energy is included in the calculation the entire set of levels moves up in energy approximately $50kT$. The levels for $g = 130$ are rezeroed against the $g = 129$ level and we get the set of energy levels shown in the third column of Fig. 3. We find that there is significant relative movement in the levels as the various structures relax differently under the influence of strain. The most important thing to notice, however, is that there is no level crossing. None of the alternate configurations is able to undergo enough strain relaxation in order to drop down below the standard configuration. The structural relaxation made possible by breaking one bond is insufficient to make up the energy lost when the bond is broken. Hence, this standard configuration still appears to be the most energetically favorable structure. If a lower energy configuration is to be found, it will have to involve a much more substantial change in structure, such as the replacement of one or more five-membered rings by six-membered rings.
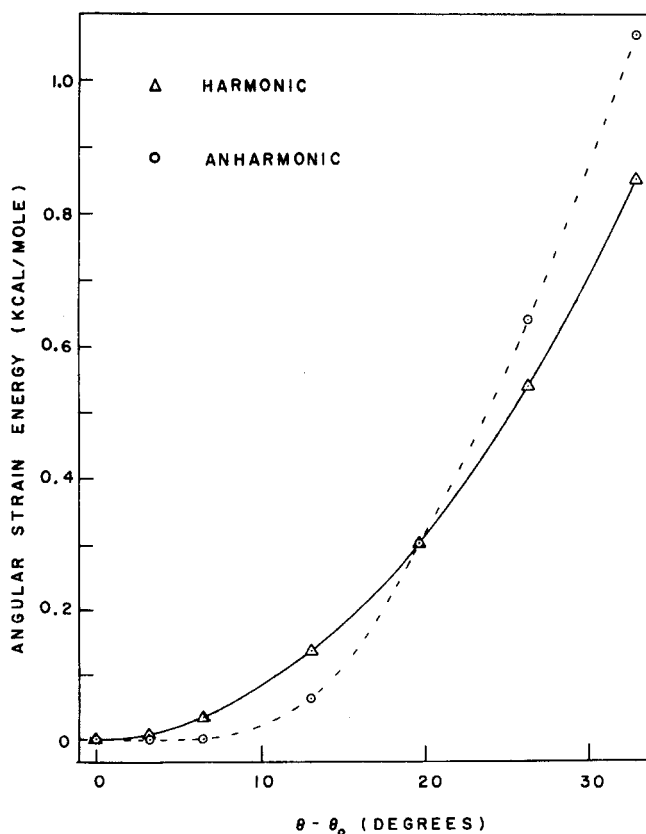

FIG. 4. Harmonic and anharmonic bond bending potentials vs
angle deformation.

for a pentamer, etc.

We wish to examine the effect of an anharmonic bond bending potential on the strain energy. In order to construct an anharmonic potential we fit a polynomial of the form

$$E_\theta = Aq^4 + Bq^6 + Cq^7$$

(where $q = \cos\theta - \cos\theta_0$ and θ_0 is the equilibrium value of the bond angle) to the change in binding energy of the dimer as the hydrogen bond is bent through an angle θ.[26] For this study the hydrogen bond was bent by rotating the proton-donor molecule in such a way that its plane always contained the symmetry axis of the acceptor molecule. The above polynomial was chosen because it gives the best fit with the fewest terms. We find $A = 38.8$ kcal/ mole, $B = -216$ kcal/mole, $C = 226$ kcal/mole for $q > 0$ and $A = 50.6$ kcal/mole, $B = -237$ kcal/mole, $C = -232$ kcal/mole for $q < 0$. A plot showing the behavior of this potential in comparison to the harmonic potential is shown in Fig. 4. The anharmonic curve is shallow near zero distortion, equals the harmonic potential near $20°$, and thereafter is stronger than harmonic. This potential will lower the total strain energy for the smaller clusters since all of their angle distortions are less than $20°$. The maximum angle distortion does not exceed $20°$ until the cluster size reaches $g = 114$. After this size the anharmonic strain will begin to catch up with and eventually exceed the harmonic strain. Now this potential will suffer from error due to not accounting for nonadditivity of the hydrogen bond energies. We do not claim it to be more accurate than the harmonic potential. We only want to use it to see what effect a reasonable anharmonic potential of this shape has on the total strain energy.

We now replace the harmonic angular potential with the above anharmonic potential in the computer routine which calculates the strain energy. The structure for each cluster size is allowed to again relax under this new potential to reminimize the energy. The results are are shown on Fig. 1. The anharmonic strain is found to be always less than the harmonic strain. The difference between them reaches a maximum at the size $g = 114$ and decreases thereafter, as would be expected from the relative shapes of the two potentials.

These results show that the strain energy is very sensitive to the shape of the bond bending potential curve. This is especially true in the region where the two curves cross, in this case near the size $g = 114$. Here we find 8 kcal/mole difference in the two results for strain energy, a difference that exceeds the energy of a hydrogen bond. Hence, some additional work in the area of quantum chemistry concerning hydrogen bond potential models would be of great value.

V. CONCLUSION

In this paper we develop a method for treating the strain energy built up in small prenucleation water clusters. For the structure of the cluster we use the molecular model of Plummer and Hale.[20] This structure is allowed to relax to minimize the strain energy resulting from hydrogen bond stretching and bending. The strain energy is evaluated for various cluster sizes up to 130 molecules. We find that the strain makes a significant contribution to the total free energy of formation of the cluster. The major contribution to the strain energy comes from hydrogen bond bending, with the minor contribution coming from bond stretching. The distribution of strain energy within the cluster agrees qualitatively with the liquid drop model, i. e., stretching or tension on the surface and compression in the bulk. For the largest cluster, changes in configuration were investigated to search for an alternate structure with a lower free energy. None was found. The effect of anharmonic terms in the bond bending potential was investigated and found to be significant.

Another problem related to the one discussed here and which, also, is crucial to atmospheric phenomena deals with the rate of growth of the various crystallographic planes of an ice surface as a function of the thermodynamic conditions to which the ice crystal is exposed. It does not seem reasonable that the perfect crystallographic lattice should propagate to the geometric surface, where it would present an extremely high free energy surface. Rather, we would expect the structure to relax at the surface to form a transition layer in which additional surface hydrogen bonding competes against lattice strain. This has been indicated by a variety of experimental evidence.[27] The technique developed here to handle structural strain can and is being used to study this ice surface problem.

ACKNOWLEDGMENTS

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