

A comparison of rigid and flexible water models in collisions of monomers and small clusters

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In this study we have investigated the dynamics of small water clusters using microcanonical molecular dynamics simulations. The clusters are formed by colliding vapor monomers with target clusters of two and five molecules. The monomers are sampled from a thermal ensemble at $T=300$ K and target clusters with several total energies are considered. We compare rigid extended simple point charge water with flexible counterparts having intramolecular harmonic bonds with force constants 10^3 and 10^5 kcal/(mol Å²). We show that the lifetimes of the clusters formed via collision process are similar for the rigid model and the flexible model with the bigger force constant, if the translational temperatures of the target cluster molecules are equal. The model with the smaller force constant results in much longer lifetimes due to the stabilizing effect caused by the kinetic energy transfer into internal vibration of the molecules. This process may take several hundreds of picoseconds, giving rise to time-dependent decay rates of constant-energy clusters. A study of binary collisions of water molecules shows that the introduction of flexibility to the molecules increases the possibility of dimer formation and thus offers an alternative route for dimer production in vapors. Our results imply that allowing for internal degrees of freedom is likely to enhance gas-liquid nucleation rates in water simulations. © 2006 American Institute of Physics.

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I. INTRODUCTION

Water vapor has a central role in atmospheric processes. Due to its ability to absorb infrared radiation, water acts as an efficient greenhouse gas and thus regulates the earth's heat balance. On the other hand, water vapor can nucleate in atmospheric conditions in the presence of a suitable secondary conucleating molecular species, such as sulfuric acid, to produce new particles. This latter process is generally thought to occur via multicomponent homogeneous nucleation, which means the spontaneous appearance of small molecular aggregates in the vapor. Water can also condense heterogeneously on preexisting particles to form cloud droplets.

Advances in computer technology in recent years have allowed molecular level studies on nucleation. Most notably, molecular dynamics (MD) has proven a valuable method, since the nonequilibrium nature of nucleation is not well captured in its entirety by methods relying on equilibrium conditions or bulk thermodynamics. On the downside, MD is very taxing on computer resources, and it is not at all clear how the intermolecular (or intramolecular) potential model should be chosen for reliable assessment of the most important quantity in nucleation, the nucleation rate.

Molecular dynamics simulations of water nucleation are relatively scarce to date and comparison of water models suitable for nucleation on the basis of published results is difficult. Of the popular choices for water potential, Yasuoka and Matsumoto¹ used TIP4P model in their MD simulations. A study by Schenter *et al.*² employed variational transition

state theory and Dang-Chang potential to perform simulations of cluster formation and decomposition. Using Monte Carlo (MC) methods, a recent comparison of water models in nucleation has been presented by Merikanto *et al.*,³ who observed that TIP4P model was the best when simulated and observed nucleation rates were compared. However, nucleation rate is dependent on the kinetics of cluster formation in a way that is never fully incorporated in the equilibrium assumption of MC. In the kinetic picture, the nucleation rate is governed by the propensity of molecules to condense on and evaporate from clusters. This imposes additional demands on the water model, because the condensation and evaporation rates are presumably related to energy transfer mechanisms during the formation and the subsequent evolution of a cluster.

In this work we investigate the effects of intramolecular degrees of freedom on cluster dynamics. The water molecules in typical simulations of water or aqueous mixtures are usually assumed to be completely rigid. Such water models reproduce one or several of the bulk properties of water (such as density, liquid structure, dielectric constant, etc.) reasonably well,⁴ although often as a result of fitting of model parameters to a particular property. Taking intramolecular motions (flexibility) into account adds little to the performance of these models⁴ (a recent study, however, reports improved liquid state properties with a novel parametrization⁵). In collision dynamics the opposite could well be true, because some of the translational kinetic energy of the incoming vapor monomer might be converted into internal vibration of the cluster molecules.

To assess the role of internal degrees of freedom in gas-

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liquid nucleation, we study formation and disruption of water clusters composed of rigid or flexible molecules. We place special emphasis on the lifetimes of clusters. While the growth of clusters may be seen as a straightforward process of attachment of monomers on a cluster, the growth rate can decrease considerably if the cluster decays before a new monomer has a chance to collide with it. A cluster with a short lifetime is not likely to participate in the nucleation process. Our aim is to perform similar molecule-cluster collision simulations for water as we did earlier for Lennard-Jones (LJ) clusters⁶⁻⁸ and highlight the differences in cluster dynamics when appropriate.

II. MODELS AND SIMULATION METHODS

Water molecules used in our simulations are based on the extended simple point charge (SPC/E) model,⁹ where flexibility is added to intramolecular bonds. The bonds are assumed harmonic with bonding potential

$$V(r) = 0.5k(r - r_0)^2, \quad (1)$$

where k is force constant and r_0 is the equilibrium bond length. The bond between the hydrogen atoms is added to constrain the H-O-H angle. A more accurate potential would take into account differences in stretching between dissimilar atoms (or equivalently stretching of O-H bonds and H-O-H bond angle) and possibly anharmonicity. In this respect our model differs from the original SPC/F model by Toukan and Rahman¹⁰ and later variants. However, since we are interested of the qualitative role of flexibility in cluster dynamics and not of exact reproduction of intramolecular vibration frequencies, the simpler model is sufficient to our purposes.

We consider three different choices for the force constant: $k=10^3$ kcal/(mol Å²), $k=10^5$ kcal/(mol Å²), and $k=\infty$. The first one is close to the commonly used values for H-O bonds.¹¹ The second one is an arbitrary choice and represents a hundredfold increase in force constant. Molecules with $k=\infty$ correspond to completely rigid water. In practice, one would expect models with $k=10^5$ kcal/(mol Å²) and $k=\infty$ to give identical results. We note that the SPC/E model with the intramolecular potential of Eq. (1) and $k=10^3$ kcal/(mol Å²) was used in simulations of small water and sulfuric acid clusters by Ding *et al.*¹²

Each individual simulation run consists of a vapor monomer colliding with a target cluster. The vapor monomer is initially placed at the average distance of 30 Å from the center of mass (c.m.) of the target cluster (this distance was varied up to 5%) and rotated to a random orientation with a given impact parameter b . The monomer is then allowed to approach the cluster and, if a new cluster is formed, the simulation is continued until the cluster breaks down. The cluster is considered intact when an oxygen atom in a molecule has at least one neighboring oxygen atom within the distance of 6.332 Å, which is twice the LJ parameter for oxygen. In case the escaping monomer (or larger fragment) rejoins the cluster, the simulation ends only when 20 ps has passed since the cluster breakdown. The incoming vapor

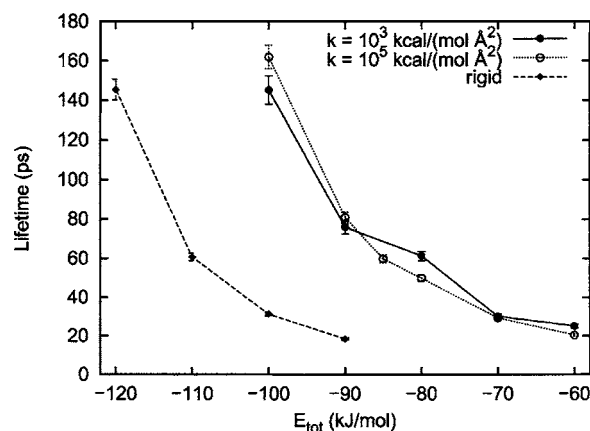


FIG. 1. Lifetime of clusters resulting from 5+1 collisions as a function of total energy of the target cluster. The force constant is given in the legend. Impact parameter is $b=0$ Å.

monomers (1000 in total) are taken from a thermal ensemble corresponding to temperature $T=300$ K. While the vapor certainly has a definite temperature, the temperatures of the nucleating clusters are not known in advance¹ and may not be well defined at all for the smallest clusters.¹³ We therefore created several sets of target cluster configurations where each set contains 1000 configurations of constant total energy, which is a well-defined quantity for all cluster sizes. The target cluster configurations were sampled from very long simulation runs of isolated clusters. A check of molecular speeds showed that, although the target clusters are small, the speed distribution of molecules was Maxwellian in shape.

The simulations were done with fixed total energy (*NVE* simulation) not to cause artificial disturbances to the cluster dynamics. This means we explicitly exclude collisions with carrier gas molecules. Trajectories were integrated using velocity-Verlet algorithm. For flexible models time steps of 0.5 fs were used in intermolecular and 0.05 fs in intramolecular motions. The rigid model was integrated with a time step of 1 fs and the intramolecular degrees of freedom were constrained using the RATTLE algorithm.¹⁴

III. RESULTS AND DISCUSSION

A. Condensation and cluster lifetime

In our earlier studies of LJ clusters we related the simulated values of cluster lifetime, evaporation rate, etc., to the total energy of the target cluster E_{tot} . Here, the same approach is possible, but not very productive when different water models are compared. This matter is illustrated in Fig. 1, where the total energy dependence of the average lifetime of the clusters resulting from collisions of monomers with five-molecule target clusters (5+1 collision) is shown. The impact parameter was $b=0$ Å in each simulation run and the lifetime was averaged over 1000 simulations for each total energy value. In a qualitative sense we get similar results as for LJ clusters:⁶ the lifetime increases with decreasing total energy of the target clusters. However, using flexible water with $k=10^5$ kcal/(mol Å²) and rigid water very dissimilar lifetimes are obtained, which is contrary to expectations; in

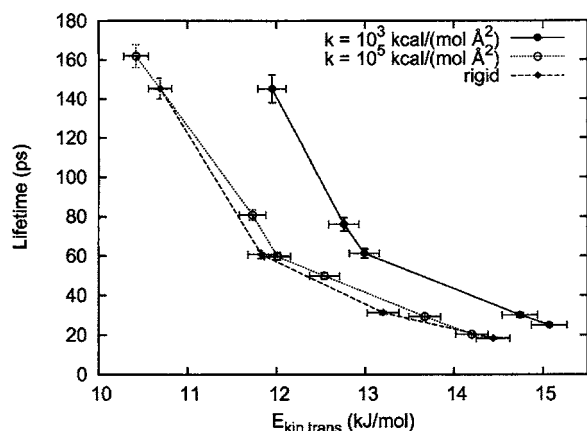


FIG. 2. Lifetime of clusters resulting from 5+1 collisions as a function of the translational kinetic energy of the target cluster.

the former case the force constant is so large that the effect of internal vibrations on dynamics should be very small. The point here is that while the energy transfer between intra- and intermolecular degrees of freedom is negligible, there is energy in intramolecular vibrations, which makes the total energy different in those two cases. The same problem is encountered if one tries to map the lifetime as a function of kinetic energy E_{kin} , because intramolecular vibrations are included in E_{kin} .

A more proper and easily implemented way to compare the water models is to consider the movement of each molecule as a whole, that is to record the kinetic energy of the c.m. of each molecule to obtain the translational kinetic energy of cluster molecules $E_{kin,trans}$. This also makes it possible to connect the simulation results to cluster temperature (or the temperature parameter related to $E_{kin,trans}$). Now, however, $E_{kin,trans}$ of the target clusters must be measured. We soon found out that $E_{kin,trans}$ exhibited sudden changes from one local minimum with some average value to another local minimum with relatively long residence times at some minima (up to several nanoseconds). These correspond to metastable states in the cluster structure. Although we are confident that our target clusters represent a fair sampling of these states, average $E_{kin,trans}$ of all the clusters over a very long time period does not give the correct picture of cluster energetics in the collision simulations. The ability of the target cluster to absorb the monomer depends primarily on the state of the cluster at the very moment of the collision and, in this respect, the earlier history of the cluster is of lesser importance. Therefore, we recorded $E_{kin,trans}$ for each target cluster just when the new cluster was formed according to the cluster definition and calculated the average of these values. The incident monomer may cause some minor changes to the target cluster prior to the collision owing to the long-range Coulombic interactions, but the effect is probably small.

The dependence of cluster lifetime on $E_{kin,trans}$ is shown in Fig. 2 for 5+1 collisions. In general, the rigid water model and the model with very stiff, but flexible bonds tend to give similar results, the lifetimes being slightly longer in the latter case. Figure 2 implies that the energy transfer to and from

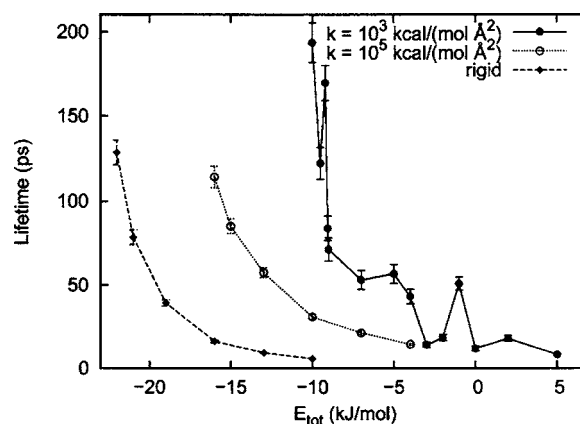


FIG. 3. Same as Fig. 1 but for 2+1 collisions.

internal degrees of freedom for molecules with $k = 10^5$ kcal/(mol \AA^2) is too slow to affect cluster dynamics. More important, however, is the observation that water molecules with the smaller force constant seem to be able to absorb some of the kinetic energy in the collision, and thus the clusters have considerably longer lifetimes.

Figure 1 shows that when the total energy of the target cluster is $E_{tot} = -80$ kJ/mol the water model with more flexible molecules yields unexpectedly long lifetimes. Such behavior, however, is absent from Fig. 2. If $E_{kin,trans}$ is compared as a function of E_{tot} linear relationship is obtained for rigid water and almost linear for water with $k = 10^5$ kcal/(mol \AA^2), but in the case of $k = 10^3$ kcal/(mol \AA^2) the clusters with $E_{tot} = -80$ kJ/mol have a diminished amount of translational kinetic energy. This particular value of E_{tot} seems to favor configurations where energy is rather stored in internal vibration of the molecules than translation.

The lifetimes of clusters resulting from collisions of monomers and dimers (2+1 collision) as a function of E_{tot} and $E_{kin,trans}$ are shown in Figs. 3 and 4, respectively. While similar conclusions can be drawn here as for 5+1 collisions, the lifetimes of clusters composed of the more flexible molecules are neither dependent on E_{tot} nor on $E_{kin,trans}$ in a straightforward manner. Indeed, as can be seen from Fig. 4, there is not even one-to-one correspondence between $E_{kin,trans}$

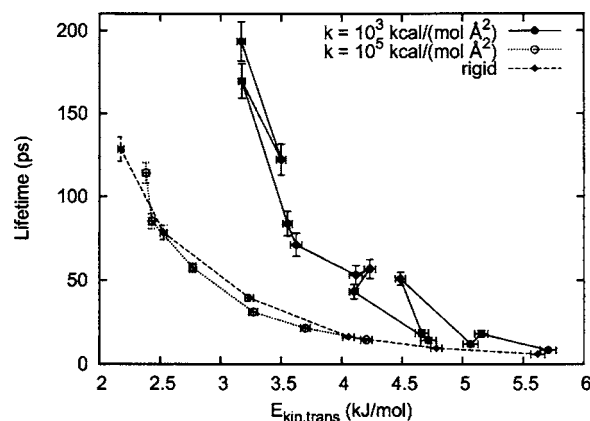


FIG. 4. Same as Fig. 2 but for 2+1 collisions. Note that the solid line connects the points in the same order as in Fig. 3.

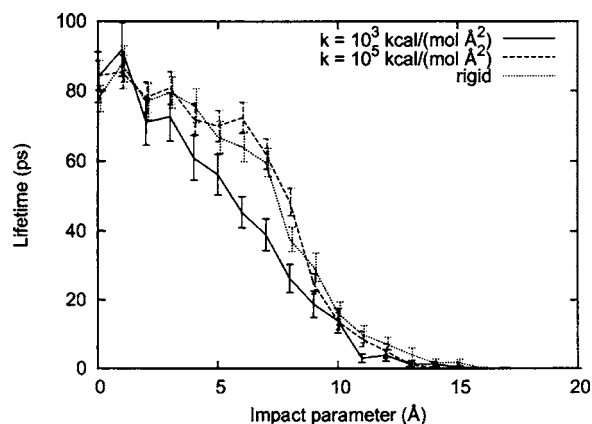


FIG. 5. Lifetime of clusters resulting from 2+1 collisions as a function of impact parameter.

and average lifetime. These results imply that with decreasing cluster size special configurations become more important in determining cluster lifetime. The lifetime curves of the other two models are smoother and resemble those we obtained for Lennard-Jones clusters.⁶

To explore the effects of collision geometry, we performed some simulations with impact parameter b ranging from 0 to 20 Å in steps of 1 Å. For comparison of the models we chose target clusters which resulted in similar lifetimes at $b=0$ Å. The results for 2+1 and 5+1 collisions are shown in Figs. 5 and 6, respectively. Although the lifetimes of clusters from dimer-monomer reactions are almost equal at $b=0$ Å for the three models, considerably lower values are obtained for the model with $k=10^3$ kcal/(mol Å²) when $b > 2$ Å. This shows that the internal degrees of freedom are more easily excited in head-on collisions; in an oblique collision the kinetic energy is likely dumped to rotation of molecules, and in this respect differences between flexible and rigid models are smaller. Note that the local maximum observed in our LJ simulations for 2+1 collisions⁶ is not seen in Fig. 5. The maximum is probably caused by the lack of internal structure in LJ atoms. The lifetime curves exhibit less obvious differences in the case of 5+1 collisions (Fig. 6), although the lifetimes seem somewhat shorter at small b and longer at larger b for the model with $k = 10^3$ kcal/(mol Å²).

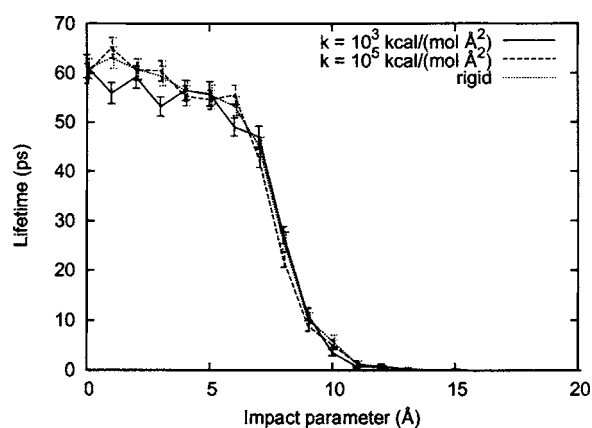


FIG. 6. Same as Fig. 5 but for 5+1 collisions.

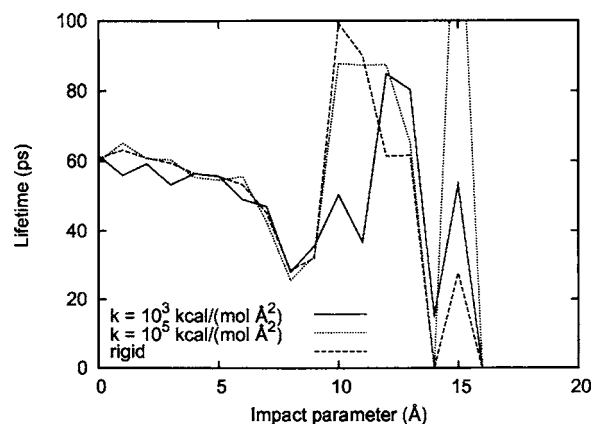


FIG. 7. Same as Fig. 6 but for successful 5+1 collisions. The error bars are omitted for clarity.

The decrease in lifetime with increasing impact parameter in Figs. 5 and 6 results from the fact that at large b most molecules pass the target cluster without actually joining it. If the cluster lifetime is recorded only when the collision is successful, meaning that a new cluster is formed according to the cluster definition, a plot like shown in Fig. 7 is obtained, where the lines correspond to those of Fig. 6. Successful collisions are rare at large values of b , which results in bad statistics, but it is quite obvious that the clusters are particularly long lived if b is greater than the radius of the target cluster. This is an expected result, because to attach the target cluster in the first place the monomer must have a curved trajectory and accordingly low velocity. Thus, a low-energy cluster with a long lifetime is produced.

A curious feature absent from our LJ simulations⁶ is the lifetime minimum at $b \approx 7-9$ Å. The cause for this is the simple cluster definition, where the nearest neighbor distance is defined via oxygen atoms. It is quite possible that the incoming monomer joins the cluster in terms of the distance between the oxygen atom in the monomer and oxygen atom in a molecule situated at the surface of the target cluster. However, the monomer in this configuration is not prone to become an actual member of the cluster, because the electrostatic repulsion between the oxygen atoms tends to expel the monomer immediately. Setting the lowest allowable lifetime to 2 ps is enough to remove the minimum with only minor changes to average lifetime elsewhere in Fig. 7. This result shows that a simple cluster definition, if applied to molecules with internal structure, may cause unexpected effects.

B. Evaporation

To study evaporation of water clusters we performed additional 5+1 simulations with the total energy of product clusters constant. Obviously, we cannot use the whole monomer library to produce such clusters, because the resulting clusters would have a large variety of total energies. Instead, we chose a monomer with the *same* c.m. velocity and total energy each time (with the initial distance and orientation varied, of course). The c.m. velocity of the monomer was chosen to correspond to the most probable velocity of water molecules at $T=300$ K. To obtain better statistics the simulation data were averaged over 10 000 collisions for each

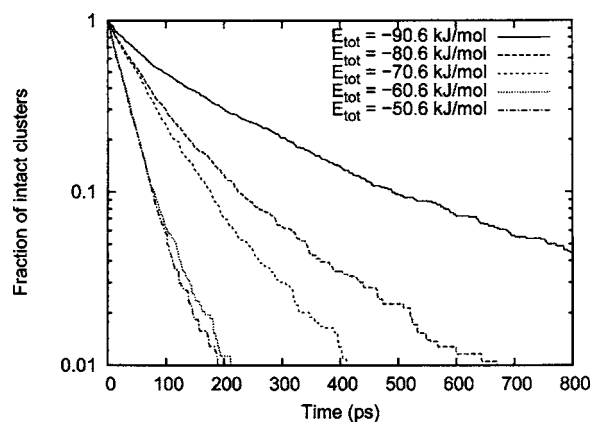


FIG. 8. The fraction of six-molecule clusters remaining intact as a function of time since the cluster formation. Flexible molecules are used with force constant $k=10^3$ kcal/(mol \AA^2). Impact parameter is $b=0$ \AA . The total energy of the clusters is shown in the legend.

total energy value. In a more realistic method the constant-energy clusters would be created from targets and monomers with different energies. Our method, however, is sufficient for the comparison of the models.

By examining the fraction of constant-energy clusters remaining intact after the collision event, we were able to show in our LJ simulations that the history of the cluster does not affect the decay probability of the cluster, as manifested by Poissonian distribution of lifetimes.^{8,15} We produced similar plots for the water models of this study. For rigid and the less flexible water we obtain Poissonian distributions, but in the case of the more flexible water a different picture emerges, as shown in Fig. 8. Instead of straight lines, upward bending curves are obtained, indicating time dependency in evaporation. This means that long-lived clusters have a smaller decay probability than short-lived clusters.

Obviously, the time-dependent evaporation behavior in Fig. 8 is related to internal vibrations of the molecules. Figure 9 shows the evolution of $E_{\text{kin,trans}}$ for six-molecule clusters with total energy $E_{\text{tot}}=-80.6$ kJ/mol and composed of molecules with force constant $k=10^3$ kcal/(mol \AA^2). The translational energy decreases over 10% during the first 400 ps and after that reaches a limiting value, indicating en-

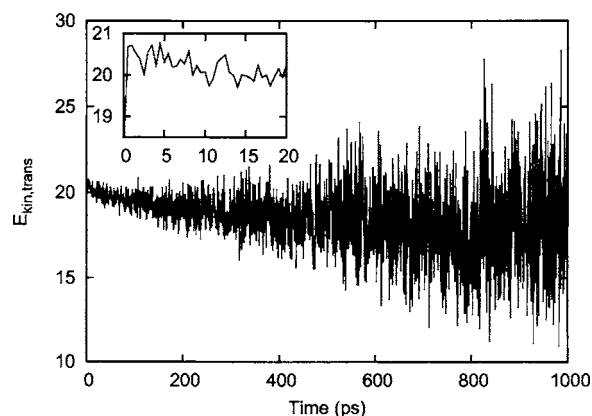


FIG. 9. Translational kinetic energy of molecules of six-molecule clusters with total energy $E_{\text{tot}}=-80.6$ kJ/mol. Force constant is $k=10^3$ kcal/(mol \AA^2). The inset shows the first 20 ps in greater detail.

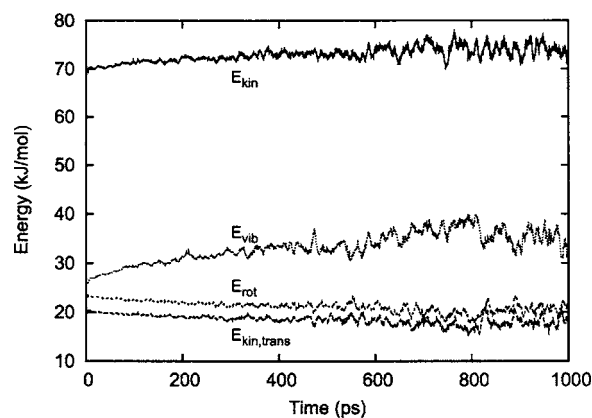


FIG. 10. Time dependence of the different energy contributions of six-molecule clusters with $E_{\text{tot}}=-80.6$ kJ/mol. Force constant is $k=10^3$ kcal/(mol \AA^2).

ergy transfer from $E_{\text{kin,trans}}$ to other forms of energy with long-term relaxation. Similar rapid transfer is also seen in rotational energy with all the models, which implies that the long-term behavior is indeed due to intramolecular vibration. Contrary to our observations of LJ systems,⁸ short-term relaxation effects are missing, as attested by the inset in Fig. 9. Neither of the flexible models show any peculiar behavior immediately after the collision, but the radius of the clusters composed of rigid molecules decreases somewhat during the first 2 ps. These kinds of effects seem to be related to the inability of rigid molecules or molecules without internal structure to rapidly redistribute the kinetic energy of the incoming monomer to other energy forms.

The long-term behavior of the different energy contributions of the clusters of Fig. 9 is plotted in Fig. 10, where the total kinetic energy E_{kin} , internal vibrational energy E_{vib} , rotational energy E_{rot} , and translational energy $E_{\text{kin,trans}}$ of the molecules are shown. To suppress fluctuations and to represent the long-term effects more clearly, only 15-point moving means of the energy values are shown. One can see that both the translational movement and rotation slow down in similar time scales. On the other hand, vibrational energy in the bonds increases substantially, a clear indication that energy is transferred to internal degrees of freedom. Kinetic energy as a whole increases as well, which implies transformation of potential energy into kinetic energy. The same kind of plots for the rigid model and the model with $k=10^5$ kcal/(mol \AA^2) does not show any long-term change in cluster energetics.

The decrease in $E_{\text{kin,trans}}$ for the model with $k=10^3$ kcal/(mol \AA^2) indicates that the velocity distribution changes in time. The distribution of c.m. speeds of the molecules at 2 and 100 ps is shown in Fig. 11. The amount of intact clusters is too small to obtain good statistics at 100 ps; nevertheless, the distribution seems to drift to lower speeds. The distribution seems Maxwellian in shape, but on the basis of the present simulations it is not possible to judge whether the temperature parameter associated with the translation of the molecules can be termed (canonical) temperature.

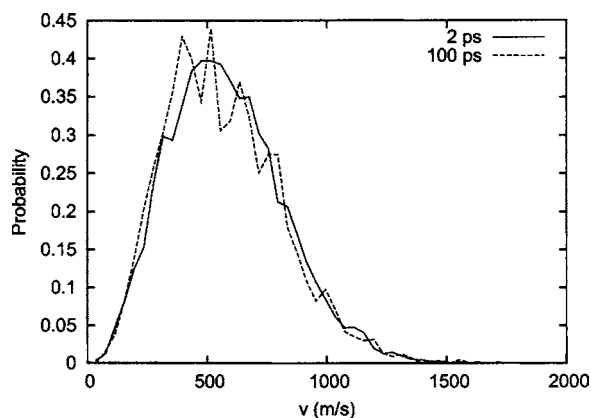


FIG. 11. Speed distribution of c.m. of molecules in six-molecule clusters at 2 and 100 ps after collision. The total energy of the clusters is $E_{\text{tot}} = -80.6$ kJ/mol and flexible molecules with $k=10^3$ kcal/(mol \AA^2) are used.

C. Bimolecular reactions

The ability of flexible water molecules to absorb some of the kinetic energy of the colliding monomer is bound to affect the efficiency of dimer production in monomer-monomer reactions. Dimers cannot be formed from the collisions of simple LJ atoms without a third body acting as a sink for the excess kinetic energy.¹⁶ Surely enough, LJ dimers with even positive total energy do exist, but they result from three-body collisions or are evaporated from clusters. Model water molecules, on the other hand, have internal structure and possibly internal degrees of freedom which facilitate the dimer production in bimolecular collisions.

Figure 12 shows the results of simulations where randomly chosen pairs of monomers from the monomer library were allowed to collide (1000 pairs for each impact parameter value). The possibility of dimer formation is considerably enhanced if flexible molecules are used. The percentages of dimers with lifetimes longer than 100 ps were 1.7% and 0.6% of all successful reactions for the flexible models with $k=10^3$ kcal/(mol \AA^2) and $k=10^5$ kcal/(mol \AA^2), respectively. Although the average lifetime of dimers is relatively low, the inclusion of flexibility in water models is likely to expedite the dimer formation in MD simulations. Note that dimers form even when rigid water is used, which

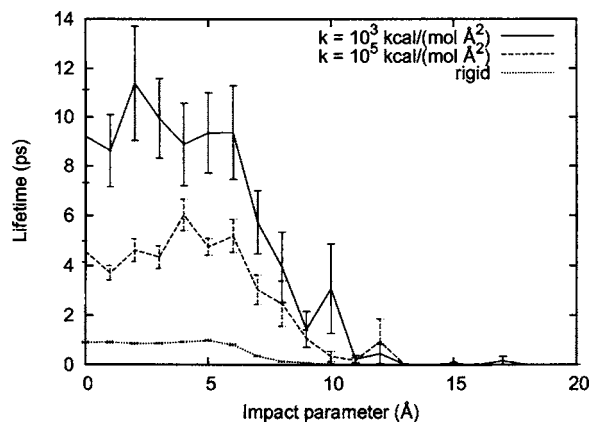


FIG. 12. Lifetime as a function of impact parameter for bimolecular collisions.

indicates that some of the translational kinetic energy can be transformed into molecular rotation. In this case the average lifetime is, however, very short; the longest lifetime observed in our simulations was 16 ps.

IV. CONCLUSIONS

In this paper, dynamics of small water clusters have been studied by MD simulations of monomer collisions with monomers, dimers, and five-molecule clusters. Rigid and flexible water models based on SPC/E water have been compared. Using the rigid water model and the model with very stiff, but still flexible bonds results in the product clusters which have similar lifetimes. In contrast, considerably more prolonged lifetimes are obtained, if a realistic amount of flexibility is introduced into the bonds.

Increasing the flexibility increases the ability of cluster molecules to transform part of the kinetic energy of the incident monomer into intramolecular vibration, resulting to a slowing down of both the translational and rotational movements of molecules. Although making the product clusters more stable, the process is rather slow: at least 400 ps is needed in collisions with five-molecule clusters for the different energetic contributions to reach their final values. The gradual energy transformation is reflected in the observed time-dependent evaporation and the slow temporal shift of c.m. velocity distributions of molecules.

The nucleation rate is intimately connected to the rates of condensation and evaporation of clusters. Since the flexibility of the molecules stabilizes the cluster as well as makes the cluster more prone to accept the vapor monomer, the nucleation rates obtained from MD simulations are likely higher if flexible molecules are used. However, when we relate the cluster properties to the translational kinetic energy of the molecules in the target cluster, we make a tacit assumption that the temperature of the target cluster does not depend on the water model (at least up to the size of the target cluster). But, as our results show, the energy transfer in a cluster composed of flexible water causes the cluster molecules to lose some of the translational kinetic energy and the cluster temperatures in simulations using the flexible model may deviate from those of the rigid model in further stages of growth. This is likely to affect the cluster distributions in the vapor and nucleation rate. Our results are then only applicable to strictly isothermal nucleation (with temperature measured from translation of the molecules). To complicate the matter, the carrier gas adds an additional stabilizing factor by removing kinetic energy from the clusters. For a comprehensive study of the effect of carrier gas and the differences in the actual cluster distributions large-scale nucleation simulations in gas phase are needed.

Finally, we have to discuss the relevance of the classical model of water. In real molecules the internal vibrations are quantized with vibrational temperatures above 2000 K for water. This means that the vibrational modes are not likely to become excited in molecular collision at 300 K. However,

some excitation is bound to happen over a long period of time, and in view of the very slow transfer of energy to vibration in our simulations, the classical model may not be completely unphysical.

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