

Molecular dynamic simulations of atom–cluster collision processes

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Monomer–cluster collisions of Lennard-Jones argon atoms have been studied using molecular dynamics simulation for target cluster sizes of 2, 3, 4, 5, 10, and 20 atoms. Capture probability of monomers by clusters and the lifetimes of the resulting clusters have been calculated as a function of impact parameter and the total energy of the target cluster. Cluster lifetime is further integrated over all impact parameters to obtain the average lifetime for each cluster size and energy. The average lifetime of the smallest aggregates is shown to be short compared to the collision time between monomers and clusters unless the vapor is highly supersaturated. The formation probability of a new cluster decreases steeply if a minimum lifetime is required for the cluster. © 2004 American Institute of Physics. [DOI: 10.1063/1.1628675]

I. INTRODUCTION

Nucleation is the mechanism by which a system relaxes from a metastable to a stable phase. A principal example is homogeneous gas–liquid nucleation, which has important applications in atmospheric sciences.¹ Gas–liquid nucleation means the appearance of tiny molecular clusters in a supersaturated vapor. If the vapor pressure is high enough, the clusters can attain a certain critical size, after which a spontaneous growth toward a bulk liquid state is possible. In a dynamical sense, gas–liquid nucleation can be thought as a series of condensation and evaporation events where the clusters gain or lose molecules. At least in principle, knowledge of the respective condensation and evaporation rate coefficients allows one to determine the homogeneous nucleation rate from a master equation governing the process.¹ It is usually assumed that in a relatively short characteristic time the system reaches a steady state condition where the cluster concentrations as well as nucleation fluxes are independent of time. The nucleation rate can then be simply expressed as a function of rate coefficients and monomer concentration. To be exact, however, nucleation is a nonequilibrium process, which involves two connected time scales. First, there exists an average time between each monomer–cluster collision. This time scale is determined by the properties of the vapor and the size of the cluster. Second, the cluster itself holds together only a finite period of time, which is related to the size and energetic properties of the cluster. Obviously, the lifetime of the cluster should be long enough in every step of the growth process for a new monomer–cluster collision to occur; otherwise the cluster is not likely to participate in nucleation.

The purpose of this work is to investigate how the probability of capture of the vapor monomer by the cluster and the lifetime of the resulting aggregate is dependent on the properties of the vapor and the target cluster, and what is the effect of the collision geometry on the process. Full understanding of these issues require an approach that takes

molecule-level detail into account. We have used molecular dynamics (MD) to simulate monomer–cluster collisions. Molecular dynamics method has a full potential to capture all dynamical aspects of the nucleation process without having to resort to any temporal or spatial averages, or to assume equilibrium conditions.

Earlier MD simulations of cluster formation and evaporation can be divided into two groups. In direct simulations the supersaturated state is achieved by quenching the vapor to a lower temperature.² Quite high supersaturations are required in this method to observe critical nuclei in reasonable time scales. The indirect technique relies on placing a pre-fabricated cluster in a supersaturated vapor and then monitoring the size evolution of the cluster.^{3,4} For our purposes, both of these methods are unwieldy because of the large number of vapor monomers involved. To reduce the system size, we decided to simulate each collision separately. In this way we also have complete control of the properties of both the cluster and the vapor monomer. However, a large number of individual simulation runs are needed to get statistically meaningful results.

A similar approach to ours was attempted earlier by Brady, Doll, and Thompson,⁵ who simulated a target cluster of 3–5 Lennard-Jones (LJ) argon atoms and calculated the capture cross sections and rate coefficients. However, they did not consider the lifetime of clusters explicitly and the generality of their result was restricted by the assumption of zero kinetic energy of the target clusters. More recently, a related work considered the collisional dynamics of water clusters.⁶

II. SIMULATION METHODS

The simulated system consists of LJ argon atoms with energy parameter $\epsilon/\kappa_B = 120.77$ K, length parameter $\sigma = 3.4$ Å, and mass 40 amu. Due to the small number of atoms in each simulation (from 3 to 21), we did not introduce any

cutoff to the LJ potential. The simulations were performed in the microcanonical ensemble using the velocity Verlet algorithm⁷ with a time step of 6 fs.

We first created a library of initial target clusters with the number of LJ atoms in the cluster $i=2, 3, 4, 5, 10,$ and 20 . For each size we generated several coordinate and velocity configurations to cover a wide range of total energies. We also created two or three independent configurations with the same size and energy for most of the clusters. In this way we were able to check that the choice of a particular initial cluster did not affect the results. We did not classify the clusters according to the kinetic or potential energy, because these are highly fluctuating quantities, especially for the smallest clusters, whereas the total energy is always accurately known. We took care that the target clusters were sufficiently long-lived not to undergo an evaporative reaction before a collision with a monomer. The shortest lifetimes in the cluster library are approximately 0.7 ns. Also, we tried to create “well-behaved” clusters which do not have occasional loose atoms, i.e., clusters which are not close to breaking up before the monomer collision.

Clusters with three or four atoms can easily assume triangular or tetrahedral configuration at low energies. We made sure that such “special” states are found only passingly in the library clusters. Nevertheless, it seems that they do not affect the results markedly, because the energy carried by the incident monomer disrupts any solidlike configuration completely. In the case of dimers, the initial configuration was set up anew at the beginning of each simulation run with the total energy randomly divided between kinetic and potential parts.

The simulation proceeds as follows. First a monomer is placed at a distance of 30 Å from a cluster with an impact parameter b and a randomly sampled initial velocity from the Maxwell–Boltzmann distribution at a fixed temperature T . This represents the coupling of the system to a thermal ensemble. To ensure statistically unbiased results the initial distance is varied a few percent and the monomer is rotated to a random orientation with respect to the center of mass of the cluster. The simulation is run until the monomer is well past the cluster (nonreactive case). If the monomer collides with the cluster (reactive case), the cluster evolution is followed for an evaporative reaction to take place or until the new cluster has stayed intact at least 1 ns. If the cluster evaporates a monomer (or a n -mer), the evolution is still followed for 10 ps in case the escaping fragment comes back. We found many cases where a monomer strayed rather far from the cluster and then rejoined it.

Monomer–cluster collisions were performed for a series of impact parameters b ranging from 0 to 30 Å with a step of 1 Å and with 1000 individual simulation runs for each b . Most of our simulations were carried out at 80 K, but we also did some simulations at different temperatures ranging from 60 to 100 K.

We used Stillinger cluster definition⁸ with the nearest neighbor distance of 2σ . This is larger than the usually assumed value 1.5σ . However, the smallest clusters in this study are rather loose, and the distance of 1.5σ caused repeated evaporative reactions to take place (even before the

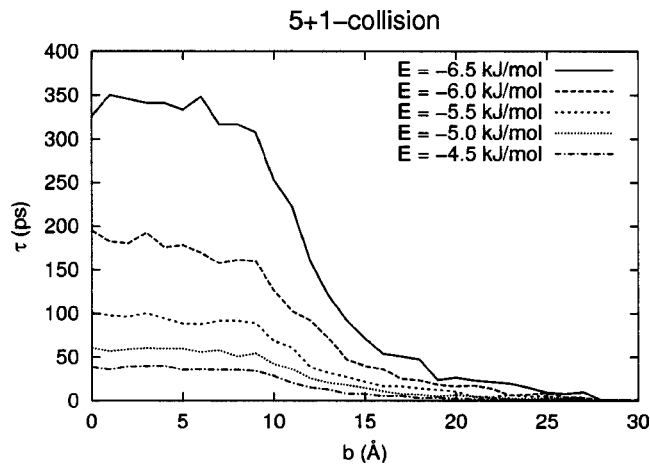


FIG. 1. Dependence of the cluster lifetime on impact parameter for collisions of a monomer with a cluster of five atoms. Temperature is 80 K. The total energy of the initial five-atom cluster is shown in the legend.

collision), which were then deemed as “false alarms” when the monomer rejoined the cluster. The implications of the larger nearest neighbor distance are discussed in the last section.

III. RESULTS

First we investigated the dependence of the lifetime τ of a cluster on the impact parameter b . The lifetime is averaged over all velocities. The results for monomer collisions with a five-atom cluster (“5+1 collision”) are shown in Fig. 1 for five different total energies of the target cluster. As expected, the lifetime is shortest for highest total energies. At large impact parameters the average lifetime approaches zero, because practically all the monomers go past the cluster. The lifetime decreases abruptly at 10 Å, which can be identified as the radius of the cluster. The location of this boundary depends on the nearest neighbor distance in Stillinger definition. Although the cluster radius is mainly a geometrical quantity, some dependence on cluster energy might be expected; however, none was found in our simulations.

The results for monomer–dimer collisions are shown in Fig. 2. Quite interestingly, the longest lifetimes are now found when the monomer is aimed close to the “boundary” of the dimer. This shows that a direct collision is likely to disrupt the dimer, which is not surprising because the monomer may have more kinetic energy than the dimer has potential energy.

The clusters in Figs. 1 and 2 have similar sizes, although the number of atoms in the clusters is different. This can be explained by the lower total potential energy of the smaller clusters, which allows the atoms to move farther from the center of mass of the cluster and, hence, the effective radius is larger than expected on geometrical grounds.

In general, if only reactive events are considered ($\tau > 0$), the longest lifetimes result from oblique collisions, because then only the slowest monomers are able to collide with the cluster and the consequent increase in the cluster energy is small. This effect is illustrated in Fig. 3, which depicts the lifetimes of clusters resulting from successful 5+1 colli-

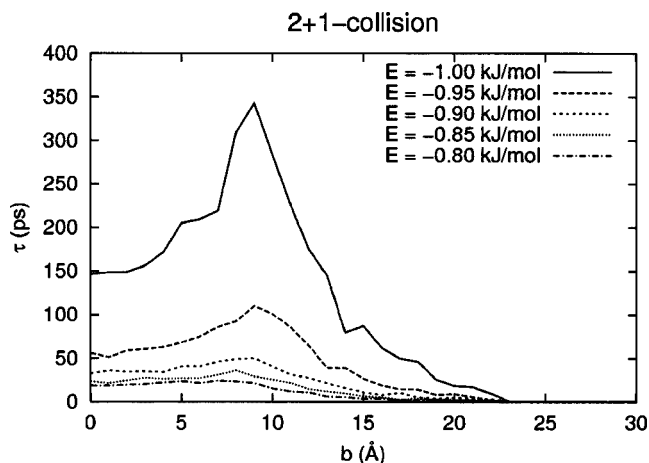


FIG. 2. Dependence of the cluster lifetime on impact parameter for dimer-monomer collisions. Temperature is 80 K. The total energy of the dimer is shown in the legend.

sions. At large impact parameters the number of successful collisions diminishes rapidly, which explains the bad statistics when b is greater than about 20 Å. This becomes apparent from Fig. 4, which depicts the probability of initially successful collisions P_s (i.e., the cluster was initially formed according to the cluster definition) as a function of impact parameter for all cluster sizes. A representative energy was chosen in each case. Practically all collisions are reactive if the impact parameter is such that the collision is geometrically inevitable. The value of P_s is slightly below one even at small b , because sometimes the interaction with the incident monomer breaks the cluster before the new cluster is formed.

The lifetime τ can be integrated over all impact parameters to give mean lifetime $\bar{\tau}$, which only depends on the cluster size, energy, and the temperature of the vapor phase. Assuming a constant flux density of monomers, the properly normalized mean lifetime is given by

$$\bar{\tau} = \frac{\int_0^\infty db b P_s(b) \tau(b)}{\int_0^\infty db b P_s(b)}, \quad (1)$$

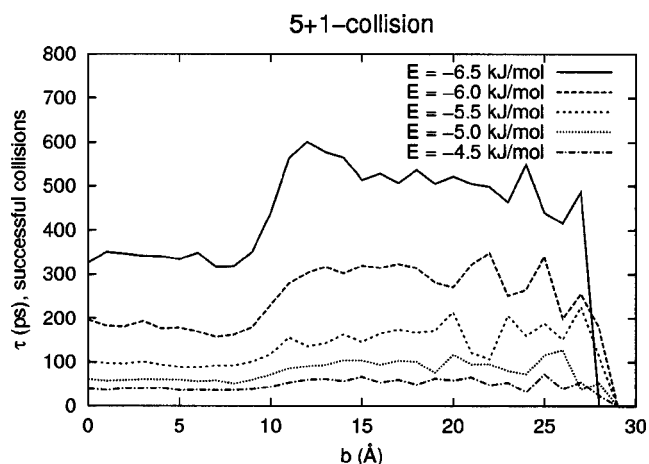


FIG. 3. Lifetime of clusters resulting from successful 5+1 collisions as a function of impact parameter. Temperature is 80 K.

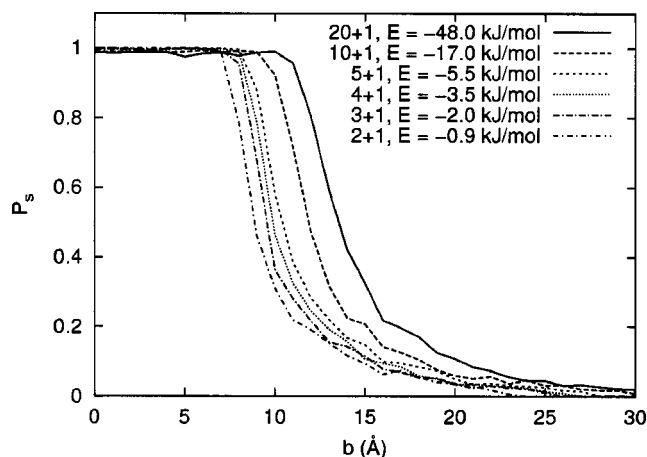


FIG. 4. Probability of successful collisions as a function of impact parameter. The size and energy of the cluster is shown in the legend. Temperature is 80 K.

where $P_s(b)$ is the probability of a successful collision.

The mean lifetime $\bar{\tau}$ as a function of the total energy of the target cluster for several cluster sizes is shown in Fig. 5. The dependence is almost linear if $\bar{\tau}$ is greater than about 100 ps. The longest lifetime for the 2+1 clusters represents the case where the target dimer was in the ground energy state with zero kinetic energy. It can be seen that, while the i clusters in the cluster library were chosen to have lifetimes of at least 0.7 ns, the lifetimes of $i+1$ clusters at the lowest points of curves are shorter typically by a factor of 10. In principle, the curves of dimers and trimers could be continued even to positive total energies. However, the resulting $i+1$ clusters have very short lifetimes and, thus, are not important in nucleation.

We also have considered the temperature dependence of $\bar{\tau}$. Figure 6 shows $\bar{\tau}$ plotted for 5+1 clusters at five temperatures ranging from 60 to 100 K. The dependence is weak and linear over the temperature range. The absolute difference between the mean lifetimes at 60 and 100 K is greatest for the cluster with the lowest energy. The relative change is approximately 10% for all energies.

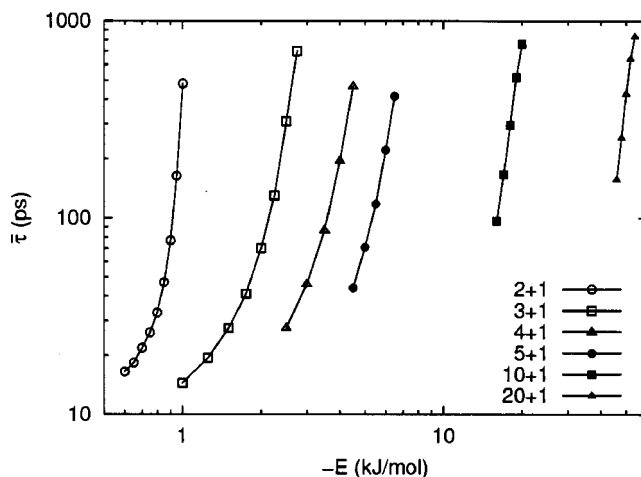


FIG. 5. Mean lifetime of clusters resulting from $i+1$ collision as function of the total energy of the i cluster. Temperature is 80 K.

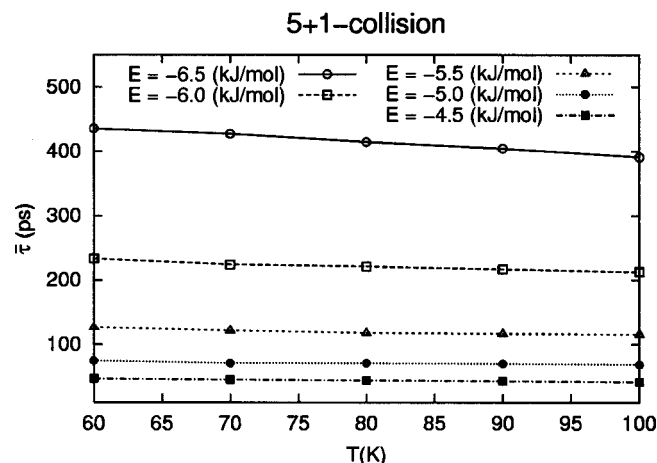


FIG. 6. Temperature dependence of the mean lifetime of 5+1 clusters. The total energy of the five-atom cluster is shown in the legend.

It is apparent from Fig. 4 that the almost all collisions at small b are successful. However, if we demand that the new cluster should have a lifetime which is longer than a specified value τ_0 , the situation changes dramatically. It is instructive to show the effect of this requirement on the probability of successful collision. To this end, we define a relative probability

$$P_r = \frac{\int_0^\infty db b P_s(b, \tau_0)}{\int_0^\infty db b P_s(b, 0)}, \quad (2)$$

where $P_s(\tau_0)$ denotes the probability of a successful collision which results in a cluster with a lifetime $\tau > \tau_0$. Figure 7 shows P_r as a function of τ_0 for 5+1 clusters. The probability drops steeply even if only a modest lifetime is required. For example, if the five-atom target cluster has a total energy of $E = -4.5$ kJ/mol, the probability that the resulting cluster of six atoms has a lifetime of $\tau_0 = 100$ ps compared to the case of $\tau_0 = 0$ ps is only about 10%.

The strong dependence of the formation probability on the cluster lifetime obviously affects the condensation coefficient. In the most general form the condensation coefficient can be written as⁶

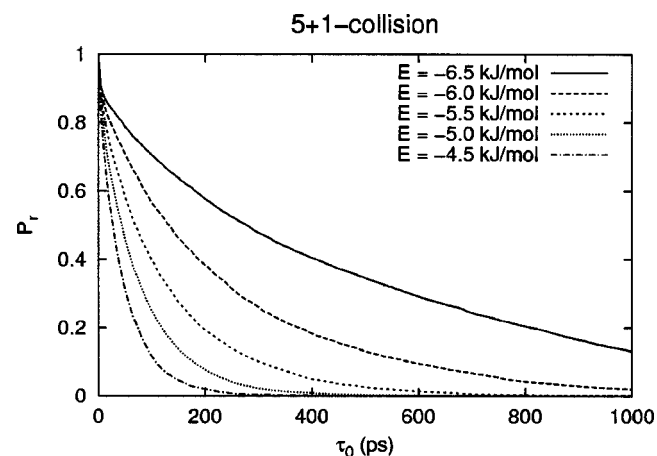


FIG. 7. Relative probability P_r as a function of the minimum lifetime τ_0 for 5+1 clusters. Temperature is 80 K.

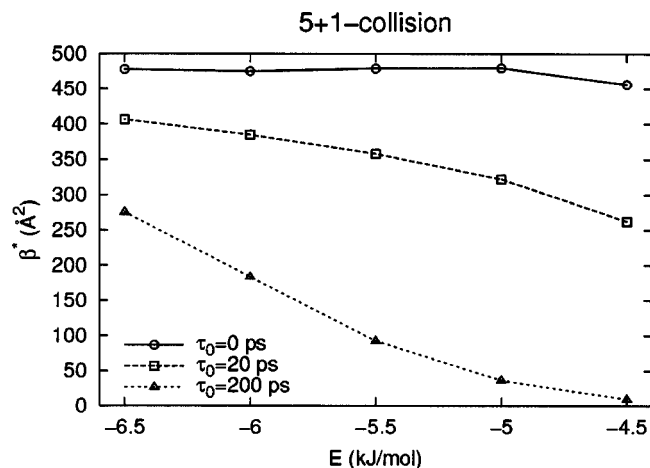


FIG. 8. The reduced condensation coefficient β_i^* as a function of total energy of the target cluster. Temperature is 80 K.

$$\beta_i = 2\pi\bar{v} \frac{N_1}{V} \int_0^\infty db b P_s(i, b, \tau_0), \quad (3)$$

where N_1 is the number of the monomers in the vapor and \bar{v} is the thermal speed. For our purposes, this equation can be better expressed as

$$\frac{\beta_i V}{N_1 \bar{v}} = 2\pi \int_0^\infty db b P_s(i, b, \tau_0) \equiv \beta_i^*, \quad (4)$$

where β_i^* can be called a reduced condensation coefficient. In the first equality the quantities on the left-hand side depend only on the properties of the vapor, while the right-hand side is related to the collision process itself. The actual condensation coefficient can readily be obtained at an arbitrary supersaturation once the integral in Eq. (4) is calculated.

The reduced condensation coefficient for 5+1 processes is shown in Fig. 8 as a function of the total energy of the target cluster. If the lifetime is not included to calculation of β_i^* , i.e., it is only required that the new cluster is formed according to the cluster definition, the condensation coefficient is practically independent of the energy of the target cluster. In this case β_i^* is determined by the collision geometry alone. However, if a certain minimum lifetime is demanded, the condensation coefficient is a function of both the energy and the lifetime limit. The lowest values of β_i^* are then found at the highest energies of the target cluster.

IV. DISCUSSION

In this paper we have simulated monomer-cluster collisions in LJ argon systems with the condensational process in mind. We have obtained results for probability of formation of new clusters, the lifetime of the clusters, and the condensation coefficient as a function of the target cluster, colliding monomer and collision geometry.

Our major findings concern the lifetime of clusters. Compared to the target clusters, the resulting $i+1$ clusters are usually very short-lived. This suggests that the probability for another vapor to collide with the cluster before it breaks up is rather low. The mean time between the collisions of monomers and clusters is given by the inverse of the

condensation coefficient, which can be approximated for LJ argon as $\beta_i^{-1} \approx 2/(p^* i^{2/3})$ ps, where $p^* = p\sigma^3/\epsilon$ and p is the pressure of the vapor. The estimated time between collisions of dimers and monomers at the saturation vapor pressure of argon at $T=80$ K [40.7 kPa (Ref. 10)] is about 1 ns. For clusters of 20 atoms collisions occur about every 250 ps. Obviously, the intercollisional period for the smallest aggregates is far too long for the nucleation to proceed at low supersaturations. In direct nucleation simulations of LJ argon the supersaturation is typically 5 or more.²

One might ask how our results are affected by the rather arbitrary choice of nearest-neighbor distance in the cluster definition. Quantities such as lifetime $\tau(b)$ and the location of the cluster boundary certainly grow if the nearest neighbor distance is increased. However, normalized quantities, e.g., $\bar{\tau}$, change much less because both the numerator and denominator are increased (or decreased) and the effects from these two very nearly cancel out each other. We found that if the nearest-neighbor distance is changed from 2σ to 1.5σ , the change in $\bar{\tau}$ is negligible.

We have restricted our considerations to small LJ clusters. The critical cluster size at reasonable supersaturations is around 50 atoms.⁴ Based on our simulations we can make some deductions on the properties of larger clusters. Our largest clusters (21 atoms) have lifetimes which compare favorably with the average time between monomer-cluster collisions. We then expect that for critical-size argon clusters the cluster lifetime is not an important factor. However, the situation can be quite different for a molecular system which has considerably smaller critical cluster size.

It should be noted that in real nucleation experiments the vapor consists of the nucleating substance and a carrier gas which acts as a heat sink. The effects of the carrier gas are not included in our simulations.

In this work we have only considered the condensational aspect of the nucleation process. Evaporation of argon clusters has been studied elsewhere.¹¹⁻¹⁶ At this point we have not tried to calculate the actual nucleation rates, although this should be the ultimate goal of the approach we have used. As a next step we aim to apply the present method to systems with more complex molecules (e.g., water) and mixtures. The generality of the results of this study will be assessed by comparing them with other molecular systems.

ACKNOWLEDGMENT

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- ¹J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (Wiley, New York, 1998).
- ²K. Yasuoka and M. Matsumoto, *J. Chem. Phys.* **109**, 8451 (1998).
- ³D. Zhukhovitskii, *J. Chem. Phys.* **103**, 9401 (1995).
- ⁴K. Laasonen, S. Wonzak, R. Strey, and A. Laaksonen, *J. Chem. Phys.* **113**, 9741 (2000).
- ⁵J. W. Brady, J. D. Doll, and D. L. Thompson, *J. Chem. Phys.* **71**, 2467 (1979); **73**, 2767 (1980).
- ⁶G. K. Schenter, S. M. Kathmann, and B. C. Garrett, *J. Chem. Phys.* **116**, 4275 (2002).
- ⁷D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, New York, 1996).
- ⁸F. H. Stillinger, *J. Chem. Phys.* **38**, 1486 (1963).
- ⁹J. Barrett, *J. Chem. Phys.* **116**, 8856 (2002).
- ¹⁰*CRC Handbook of Chemistry and Physics*, 83rd ed., edited by D. R. Lide (CRC Press, Boca Raton, 2002).
- ¹¹A. Rytönen, S. Valkealahti, and M. Manninen, *J. Chem. Phys.* **106**, 1888 (1997).
- ¹²V. M. Bedanov, *Mol. Phys.* **69**, 1011 (1990).
- ¹³R. W. Smith, *Z. Phys. D: At., Mol. Clusters* **21**, 57 (1991).
- ¹⁴C. E. Román and Garzón, *Z. Phys. D: At., Mol. Clusters* **20**, 163 (1991).
- ¹⁵C. Rey, L. J. Gallego, M. P. Iñiguez, and J. A. Alonso, *Physica B* **179**, 273 (1992).
- ¹⁶S. A. Harris and I. J. Ford, *J. Chem. Phys.* **118**, 9216 (2003).