On possible simplifications in the theoretical description of gas phase atomic cluster dissociation

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In this work, we investigate the possibility of describing gas phase atomic cluster dissociation by means of variational transition state theory (vTST) in the microcanonical ensemble. A particular emphasis is placed on benchmarking the accuracy of vTST in predicting the dissociation rate and kinetic energy release of a fragmentation event as a function of the cluster size and internal energy. The results for three Lennard-Jones clusters (LJₙ, n=8,14,19) indicate that variational transition state theory is capable of providing results of accuracy comparable to molecular dynamics simulations at a reduced computational cost. Possible simplifications of the master equation formalism used to model a dissociation cascade are also suggested starting from molecular dynamics results. In particular, it is found that the dissociation rate is only weakly dependent on the cluster total angular momentum \( J \) for the three cluster sizes considered. This would allow one to partially neglect the \( J \)-dependency of the kinetic coefficients, leading to a substantial decrease in the computational effort needed for the complete description of the cascade process. The impact of this investigation on the modeling of the nucleation process is discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3078449]

I. INTRODUCTION

The nucleation of a new phase is of fundamental interest in several fields of science, spanning a range including the study of atmospheric phenomena, the possible application to building nanostructures via chemical vapor deposition and the formation of critical germs during crystallization. Even though the thermodynamics of the process seems to have a robust conceptual basis, the phenomenon appears less clear at the molecular level. In fact, the relevant time scales involved in the process of phase formation are still under intense investigation.

In this field, the condensation of a liquid phase starting from a homogeneous supersaturated vapor has received considerable attention from the theoretical chemical physics community during the past few years, perhaps because it might be considered as a simple (but not trivial) representative case of this family of processes. As a consequence, the past decade has witnessed a surge of contributions devoted to improving the understanding of the process time scales, with many studies focusing on the large scale calculation of nucleation rates by means of molecular dynamics (MD),1-4 on the benchmark of currently available theories (e.g., classical nucleation theory, extended liquid drop model, dynamical nucleation theory, and other semiphenomenological models),1,2,5 and on the calculation of the work necessary to build a cluster from the supersaturated vapor.6,7

Despite these efforts, the routine application of computational approaches to the calculation of nucleation rates for experimentally relevant systems still appears as a distant goal, the exception being perhaps the prediction of the critical cluster size that can be done by means of thermodynamic integration.6 As far as MD simulations are concerned, the main reason for the currently limited applicability is the necessity of simulating large systems with a high degree of supersaturation to witness a condensation event within a reasonable time span. It is therefore in this context that the framework provided by dynamical nucleation theory (DNT), introduced by Schenter et al.,8 represents an appealing possibility to tackle the same task. In doing so, DNT follows closely the ideas provided by the Szilard model and deals only with two events, namely, the dissociation and condensation of single particles from and to a cluster at constant temperature \( T \).

\[
\begin{align*}
&M_n \rightarrow M_{n-1} + M, \\
&M_{n-1} + M \rightarrow M_n,
\end{align*}
\]

where \( k^d_n(T) \) and \( k^c_{n-1}(T) \) are the dissociation and condensation rates, respectively. If this was known for the relevant cluster sizes, the time evolution of a nucleating vapor at constant temperature could be predicted using a set of coupled kinetic equations describing \( N(n,T) \), the time dependent \( M_n \) cluster population. In the case of single monomer evaporation/condensation, this set reads

\[
\frac{dN(n,T)}{dt} = k^c_{n-1}(T)N(1,T)N(n-1,T) + k^d_{n+1}(T)N(n+1,T) - k^d_n(T)N(n,T) - k^c_n(T)N(1,T)N(n,T),
\]

where we have explicitly indicated the dependency on the temperature \( T \) of the system and deviated from the usual convention of using the dissociation \( (a) \) and condensation

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(β) coefficients in order to be consistent with the standard chemical kinetics notation. A more general framework than Eq. (3) would be represented by the master equations (MEs) approach,9 which would be better suited to follow the time dependent evolution of \( N(n,T) \) in more complex cases (e.g., when the single moiety dissociation-association process constraint is lifted9), or whenever additional variables are required to describe the system. Starting from Eq. (3), DNT focuses mainly on computing the dissociation rate \( k_d^n(T) \) of the \( n \) molecule cluster \( M_n \) by means of canonical variational transition state theory (vTST). The equilibrium cluster populations \( N(n,T) \) (or the free energy difference \( \Delta F_{n,n-1} = F_{n} - F_{n-1} \)) and detailed balance are then used to estimate the rate \( k_{n-1}^c(T) \) for the inverse condensation process.

In term of its emphasis, DNT differs substantially from other methods that compute \( k_{n-1}^c \) by means of simple collision theory arguments and successively estimate \( k_d^n \) using the former quantity and the relevant equilibrium constant (for instance, see Ref. 10, and references therein). Unfortunately, methods relying on collision theory are forced to assume a radius \( r_p \) for \( M_n \) in order to estimate the monomer-cluster cross section in a simple and computationally inexpensive way. Clearly, this introduces a degree of arbitrariness that is not present in DNT, where \( r_p \) is instead derived directly from vTST arguments as the location \( r_n^* \) of the spherical separatrix that minimizes the reactive flux. This theoretical advantage, however, is obtained at the price of an increased computational cost (i.e., the one required to estimate \( k_d^n \)), a fact perhaps suggesting the need for the development of efficient simulation methods to tackle the task of computing cluster dissociation rates. As a support for this idea, we mention the fruitful attempt made by Crosby et al.11 to speed up the calculation of \( k_d^n \) within the DNT framework.

In considering the usage of Eq. (3) to describe the system time evolution, it is easy to realize that both \( k_d^n \) and \( k_{n-1}^c \) could, in principle, be exactly computed using molecular dynamics (MD) without employing statistical theories. The latter, however, provides a computational advantage with respect to MD, which becomes inefficient in computing \( k_d^n \) for low temperature (T) or energy (E) clusters. Notice that the choice of the ensemble (i.e., constant T or E), first, depends on the specific details of the process one wishes to simulate and, second, it has an impact on the computational effort needed to study the process as will be discussed in the following. As to the former issue, the use of a constant T ensemble would be justified only for nucleating systems where a sufficiently high number of monomer-cluster collisions take place between two subsequent condensation/dissociation steps, a situation that appears likely only in presence of a sufficiently high bath gas pressure. Besides, both Harris and Ford12 and Burrett13 provided computational evidence suggesting that microcanonical MD simulations should be used to describe dissociation events due to a time dependent behavior of the canonical rate constant \( k_d^n(T) \) related to the strategy employed to maintain \( T \) constant. In the case of zero/low bath gas pressure, of relevance also for constant energy cross beam scattering experiments, the microcanonical ensemble (henceforth indicated either as \( \mu \) or NVE) appears therefore better suited for the description of condensation/dissociation events thanks to the fact that \( E \) is a constant of motion, a fact suggesting one should focus on the calculation of microcanonical rates \( \{ k_d^n(E) \} \) and \( \{ k_{n-1}^c(E) \} \). Following the time evolution of \( N(n,E) \) instead of \( N(n,T) \), however, increases the computational cost required to predict the nucleation rate due to the necessity of tracking the time evolution of both \( E \) and \( n \).

To complicate the matter further, the angular momentum (J–) resolved microcanonical ensemble (indicated as \( \mu.J \) or \( J \text{NVE} \)) should be used instead of NVE in gas phase to account for the constant of motion nature of \( J \). In this case, however, the problem with the scarce efficiency of MD in computing dissociation rates would be exacerbated due to the necessity of integrating the equations of motion for several values of \( J \), a task required not only to obtain the \( J \)-dependent behavior of \( k_d^n(E,J) \) and \( k_{n-1}^c(E,J) \) but also to predict more detailed state-to-state rates such as \( k_d^n(E \rightarrow E',J \rightarrow J') \). Here, \( E' \) and \( J' \) are the internal energy and total angular momentum of the product cluster \( M_{n-1} \), while \( k_d^n(E,J) \) and \( k_{n-1}^c(E,J) \) are the dissociation and association rates for clusters with total energy \( E \) and angular momentum \( J \).

As a consequence of this brief discussion, one should quickly realize the necessity of finding a computationally convenient approach to estimating \( k_d^n \) and \( k_{n-1}^c \), for the hope of developing a \( \mu- \) or \( J - \) ensemble based numerical scheme able to predict the time dependent behavior of a nucleating system to remain alive. Whereas estimating \( k_{n-1}^c \) is expected to be reasonably straightforward and computationally inexpensive thanks to the absence of high energy barriers between impinging monomer and clusters, computing \( k_d^n(E) \) should be more expensive than obtaining \( k_d^n(T) \). Thus, a statistical theory may, again, represent a practical way of avoiding the high computational cost of long MD simulations, provided that it is shown capable of accurately approximating \( k_d^n(E) \). An appropriate statistical theory should also provide an accurate estimate for other quantities such as the kinetic energy release (KER) (\( E_r = E_r + E_r \)) distribution,15 i.e., the probability of finding the systems after a dissociation event with the amount of energy \( E_r \) injected into relative translational energy \( E_r \) of the two fragments and the rotational energy \( E_r \) of the remaining cluster. As it should become apparent from the discussion in Sec. II, the KER is a key ingredient needed for setting up the MEs.

Results suggesting the possibility of predicting both \( k_d^n \) and the KER distribution for a dissociation event by means of statistical theories have been already presented in the past. For instance, phase space theory (PST) has been previously used to estimate \( k_d^n \) for relatively small rare gas and aluminum clusters and found to perform well. Similarly, Schenter et al.19 provided evidence that their version of canonical vTST, developed to tackle the calculation of \( k_d^n(T) \) for molecular clusters, is in agreement with MD results to within a factor of 2. More recently, Calvo and Parneix (Ref. 15, and references therein) investigated the possibility of computing both the KER distribution (i.e., the probability of \( E_r \) assuming a specific value \( e \)) and the probability of the cluster fragment to have a total angular momentum \( J' \) by means of PST, obtaining results that strongly suggested this
theory to be capable of accurately predicting both quantities. Estimating the reaction rate, however, was indicated as a more demanding task due to the necessity of computing accurately the cluster density of states $\Omega(E)$, an issue previously discussed in Refs. 13 and 18. To circumvent the latter, Calvo and Parneix20 resorted to calibrating PST dissociation rates against high energy MD simulations, a pragmatic approach that allowed them to apply PST to a sequence of cluster decays.

Apart from the computational difficulties inherent in obtaining $\Omega(E)$, another complication is present in the use of PST for the calculation of $k^d_{\text{st}}(E)$ for a range of cluster sizes, namely, the definition of the asymptotic potential $V_{\text{asym}}(r)$ describing the region of the loose transition state due to relative orbital motion of the two dissociating fragments. In a previous application of the theory, Peslherbe and Hase18 resorted to fitting the long range interaction between Al$_n$ for the latter quantities. Given the four-index KER distributions. One of the aims of this work is therefore to extend this approach to apply PST to a sequence of cluster decays.

Section III begins by describing a numerical investigation of the reaction rate $k^d_{\text{st}}(E)$ for selected dissociation processes. Such an investigation is therefore necessary in order to determine $k^d_{\text{st}}(E)$ for a range of cluster sizes, namely, the definition of the asymptotic potential $V_{\text{asym}}(r)$ describing the region of the loose transition state due to relative orbital motion of the two dissociating fragments. In a previous application of the theory, Peslherbe and Hase18 resorted to fitting the long range interaction between Al$_n$ for the latter quantities. Given the four-index KER distributions. One of the aims of this work is therefore to extend this approach to apply PST to a sequence of cluster decays.

The outline of this manuscript is the following. In Sec. II, we briefly introduce the theoretical approach used in this work. Section III begins by describing a numerical investigation of the reaction rate $k^d_{\text{st}}(E)$ for selected dissociation processes. Such an investigation is therefore necessary in order to determine $k^d_{\text{st}}(E)$ for a range of cluster sizes, namely, the definition of the asymptotic potential $V_{\text{asym}}(r)$ describing the region of the loose transition state due to relative orbital motion of the two dissociating fragments. In a previous application of the theory, Peslherbe and Hase18 resorted to fitting the long range interaction between Al$_n$ for the latter quantities. Given the four-index KER distributions. One of the aims of this work is therefore to extend this approach to apply PST to a sequence of cluster decays.

Generally speaking, we wish to build on the evidence that PST provides an accurate alternative to MD and that it is equivalent to more standard vTST in the case of a loose transition state. In this respect, we begin by considering the use of the TST equation for the classical statistical rate of a dissociation process at constant energy $E$

$$k^d_{\text{st}}(E) = \frac{\int S'E[H(p,q)] - E|p,q,\Gamma]}{\int S'[H(p,q)] - E|p,\Gamma}.$$

Here, $S'$ is the hypersurface in phase space separating the reactant from the product and $v_1$ is the velocity perpendicular to this surface and pointing in the direction of the products. The integral at the numerator is carried out over the transition state (state 2), whereas the one at the denominator is computed over the reactant phase space $V$ enclosed by $S'$. Often the dependence of $S'$ on the momenta $p$ is neglected and only the coordinates $q$ are used for its definition.

In the case of a simple dissociation process, Eq. (4) can be rewritten as

$$k^d_{\text{st}}(E) = \frac{\int_S[H(p,q)] - E|p,q,\Gamma]}{\int_S[H(p,q)] - E|p,\Gamma},$$

where the distance between the dissociating moieties and the center of mass of the remaining cluster is used as intrinsic reaction coordinate $(r_{IRC})$, $r_C$ is the critical distance for IRC (i.e., the location of a spherical $S'$), and $r_{IRC}$ is the relative velocity of the two dissociating fragments along $r_{IRC}$. According to the usual vTST prescriptions, $r_C$ must be chosen such that $k^d_{\text{st}}(E)$ is minimum. Notice that our choice of reaction coordinate is expected to be adequate at low-medium energies, i.e., when the remaining cluster, although fluxional, is still fairly compact. At higher energies, the presence of wide excursions of the surface particles may induce the disappearance of the minimum in $k^d_{\text{st}}(E)$ as a function of $r_C$, preventing one from obtaining a theoretically sound estimate for the dissociation rate constant. This difficulty may, however, be cured with a different choice for $r_{IRC}$.

Assuming $H(p,q) = 1/2\sum_{i=1}^{n}p_i^2/m_i + V(q)$, the kinetic energy of the system is diagonal in Cartesian coordinates and the integrals in Eq. (5) can be separated obtaining

$$k^d_{\text{st}}(E) = \frac{\int [H(V(q)) - 1/2\sum_{i=1}^{3n-5/2}V(q)]|\Gamma_{IRC}\rangle_{K}dq}{\int [H(V(q)) - 1/2\sum_{i=1}^{3n-5/2}V(q)]dq},$$

where $\langle V(q) \rangle$ is the potential energy surface of the system, $n$ is the number of atoms and $\langle |\Gamma_{IRC}\rangle_{K} \rangle$ is the microcanonical ensemble average of the relative velocity of the reactant $(R)$ through the critical surface in the direction of the product $(P)$ for a value of the internal (vibrational plus rotational) kinetic energy equal to $E - \langle V(q) \rangle$. Notice that $[H(V(q)) - 1/2\sum_{i=1}^{3n-5/2}V(q)]$ is the appropriate configuration weight for an isolated molecule composed of $n$ atoms as obtained by factorizing out the contribution due to the center of mass motion in the way suggested by Schranz et al.23 An alternative form for Eq. (6) is obtained by using the Heaviside function $H_-(r_{IRC})$ selecting velocities directed from $R$ to $P$ and by rewriting the integral ratio as a product of two ratios.
In this form, it is made apparent that the calculation of $k_{\text{stat}}^d(E)$ could, in principle, be separated in two (or more) parts with different interpretations. In fact, the first ratio represents the expectation value of $r_{\text{IRC}} H_{\text{IRC}}(r_{\text{IRC}})$ when the system is constrained to have the dissociating moiety at the critical distance $r_C$ (henceforth dubbed as $\mu$-TS ensemble). The second ratio, instead, is the probability of finding the system at the critical distance.

Notwithstanding the fact that $k_{\text{stat}}^d(E)$ could be estimated directly using Eq. (6) (see Ref. 24 for its original description and Ref. 25 for an alternative implementation), the definition of the $\mu$-TS ensemble introduced in Eq. (7) provides one with conceptual and computational advantages. As for the computational side, the probability of finding the system on the separatrix can be efficiently computed by employing microcanonical umbrella sampling (US) in conjunction with a new estimator for the Dirac delta recently developed by us. From the theoretical viewpoint, instead, the advantage comes from the possibility of thinking about the first integral ratio in Eq. (7) as a specific example [i.e., for $\dot{r}_{\text{IRC}} H_{\text{IRC}}(\dot{r}_{\text{IRC}})]$ of an expectation value calculation over the $\mu$-TS ensemble (for instance, see Ref. 28, where a similar factorization was previously exploited to correct for the lack of dynamical effects in TST).

From this brief discussion, it should be apparent that substituting $\dot{r}_{\text{IRC}}$ with a different dynamical observable would, in principle, give access to the phase space average of the latter when the system is constrained to lie on the separatrix while having $H_{\text{IRC}}(r_{\text{IRC}})=1$. Thus, the computational machinery developed for $k_{\text{stat}}^d(E)$ may, for instance, lend itself to the calculation of $P_n(E, \epsilon)$, the probability distribution function of finding $E_n$ in the range $[\epsilon, \epsilon + d\epsilon]$ when the reaction has a total internal energy $E$. This may be possible provided that the relevant dynamical observable $E_n$ can be written, at least, as an implicit function of the system position $q$.

A similar statement can be made for $P_n(E, \epsilon)$ when only the distribution of $E_n$ is of interest. Needless to say, the importance of $P_n(E, \epsilon)$ and $P_n(E, \epsilon)$ stems from the necessity of defining the internal energy $E'$ of the fragment cluster after a dissociation event to predict the rate of, e.g., a second monomer ejection, and it is therefore of prime interest in the description of multiple cluster decays as thoroughly discussed in Ref. 20.

To derive a mathematical definition for $P_n(E, \epsilon)$ fitting the framework provided by Eq. (7), we start by noticing that it could be approximated by the fractional number of times a system distributed according to the $\mu$-TS ensemble and with $H_{\text{IRC}}(r_{\text{IRC}})=1$ is found having $E_n$ in the narrow but finite interval $[\epsilon, \epsilon + d\epsilon]$. Within this approximation, it is implicitly assumed that no energy exchange takes place between the two dissociating moieties after an event has been dubbed as reactive. Given a specific geometrical configuration $q$ of the molecules in the system, the instantaneous amount of kinetic energy $K$ available to the latter is given by $K=E-\mathcal{V}(q)$, a part of which would be distributed into $E_n$. If $K$ is statistically distributed among degrees of freedom, the relative number of times $E_n$ falls within $[\epsilon, \epsilon + d\epsilon]$ is simply given by $(H_{\text{IRC}}(r_{\text{IRC}}) \Delta(\epsilon))_K$, where $\Delta(\epsilon)$ is a normalized rectangular distribution with nonzero values only in the interval of interest. Taking the limit $d\epsilon \to 0$ and integrating over all available configuration space with the proper microcanonical weighting [i.e., $(E-\mathcal{V}(q))^{3n-5}/2$ (Ref. 24), one arrives at

$$P_n^\mu(E, \epsilon_n) d\epsilon_n = \frac{\int_{V}(E-\mathcal{V}(q))^{3n-5}/2 \delta(E_n(q)-\epsilon_n) K dq}{\int_{V}(E-\mathcal{V}(q))^{3n-5}/2 \delta(r_{\text{IRC}}-r_C) dq}$$

Here, $E_n(q)$ explicitly indicates the dependency of $E_n$ on the atomic coordinates and $\mathcal{V}(E_n(q)-\epsilon_n)$ is used to count the number of occurrences for a specific $\epsilon_n$. In practice, Eq. (8) suggests to use a constrained simulation with $r_C$ chosen according to the variational TST principle and to estimate $P_n^\mu(E, \epsilon_n)$ by counting the number of times $E_n$ falls in the small range between $\epsilon_n$ and $\epsilon_n + d\epsilon_n$.

While employing Eq. (8) to obtain $P_n^\mu(E, \epsilon_n)$, one faces an additional difficulty related to the lack of an analytical form for $E_n(q)$. A possible way to circumvent this issue is to tackle the calculation of $(H_{\text{IRC}}(r_{\text{IRC}}) \delta(E_n(q)-\epsilon_n))_K$ numerically, i.e., by sampling the particle momenta with the appropriate distribution and subject to the constraint $K=E-\mathcal{V}(q)$ as suggested in Ref. 29. Practically speaking, the randomly sampled momenta are first used to test if $r_{\text{IRC}}$ is correctly oriented, and subsequently employed to obtain $E_n(q)$. In the latter, the $E_n$ component in the fragment cluster can be computed using its total angular momentum and the instantaneous position of its constituent atoms to define the inertia tensor, whereas $E_i$ is easily obtained from the relative velocity of the two dissociating fragments. Notice that the numerical scheme just discussed implicitly contains the effect of the
III. RESULTS AND DISCUSSION

A. Behavior of $k^N_J(E,J)$ as a function of the total angular momentum $J$

As mentioned in Sec. I, the task of modeling vapor nucleation using a set of MEs would be substantially simplified if one was allowed to neglect the dependence on the system angular momentum $J$. It therefore appears important to explore whether the weak sensitivity of $k^N_J(E,J)$ on $J$, the angular momentum of the parent cluster, suggested for LJ$_{12-14}$ (Ref. 13) and Al$_6$ (Ref. 18) is more generally valid. We reiterate that the reason for this investigation is the fact that predicting dissociation rates in gas phase would, in principle, force one to work within the framework provided by the $\mu J$-ensemble. Thus, a (partial) justification is needed for the usage of the simpler $\mu$ ensemble when there is no interest in computing the evolution of the total angular momentum or of any related observables during the process modeled (e.g., an evaporation cascade).

In order to test such a hypothesis on slightly more general grounds than provided by Refs. 13 and 18 the dissociation rates of three different LJ$_n$ clusters ($n=8, 14$ and $19$) were computed as a function of both $E$ and $J$ using MD trajectories. These three values of $n$ were selected in order to explore archetypal structural changes between reactants and products.\cite{15} In particular, $n=8$ presents substantial structural differences from its product, the latter being a high symmetry ($D_{5h}$) oblate rotor that is expected to be capable of isomerizing in the range of energies amenable to MD simulations.\cite{15} $n=14$ was instead chosen for its low evaporation energy due to its capped icosahedral structure and for the fact that it produces a spherical species, whereas $n=19$ was selected to explore the effect of breaking the compact structure of a nonspherical magic number cluster. Figure 1 shows the minimum energy structures for the clusters relevant to this study.

For all systems, the details of the simulations employed to compute the reaction rates are the following. Atoms were assumed to interact by means of a pairwise LJ potential written as $V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$, with the parameters ($\epsilon=3.7935 \times 10^{-4}$ hartree and $\sigma=6.4354$ bohr) being chosen to represent the Ar–Ar interaction. A mass of 73 350.6 times the electron mass was used for the Ar atoms. For each cluster, an initial equilibration stage was conducted at the appropriate total energy $E$ by means of a MMC simulation in the microcanonical ensemble;\cite{24} each of the atoms in the cluster was also constrained to have its distance from the center of mass of the remaining ones shorter than 4$\sigma$. Trajectories were started from statistically independent samples extracted from the MMC simulations; 10,000–25 000 total trajectories per $(n,E,J)$ triplet were employed to estimate dissociation rates. In the triplet, $E$ is the total energy of a cluster and includes the contribution from the potential energy, the rotational kinetic energy, and the vibrational kinetic energy but not from the center of mass motion. Trajectories were integrated using the leap frog algorithm and a time step of 200 a.u. (roughly 5 fs) up to a maximum of 120 ps. The total energy was conserved better than 10 ppm in all cases. Initial velocities for all particles were chosen according to the stochastic procedure suggested in Ref. 29. The total angular momentum was sampled employing a simple rejection procedure with a sampling window of six atomic units of angular momentum $h$ centered around the chosen $J$ value. To select physically sensible values for the latter quantity, short preliminary MMC simulations were carried out on each LJ$_n$ at the chosen $E$. During the MMC sampling, initial velocities for the particles were chosen as indicated above (see Ref. 29) and used to produce the probability distribution $p(J)$ for $J$ at the specific $E$. In general, such distributions are well approximated by the canonical-like density $p(J) \sim J^2 \exp[-\alpha J^2]$. The upper limit of the range of $J$ explored in the MD simulations was chosen as the value $J_{\text{upper}} > J_{\text{max}}$ for which $p(J_{\text{upper}})/p(J_{\text{max}}) \sim 0.2$, with $J_{\text{max}}$ being the position of the maximum in $p(J)$; with this choice, \int_0^{J_{\text{upper}}} p(J) dJ/\int_0^{J_{\text{max}}} p(J) dJ > 0.85$ for every $E$. As final comment, we notice that an explicit dependency on $J$ of the cluster structure and dynamics is introduced only at the beginning of the MD trajectory. However, the initial trajectory configurations partially accounts for some angular momentum effect due to the microcanonical sampling. Also, a substantial re-equilibration of the clusters is allowed by their reasonably long lifetime (see below).

During a trajectory evolution, a particle was considered...
dissociated when its distance from the center of mass of the remaining cluster was larger than 4r, a region for which the interaction potential between the two dissociating fragments was found negligible. The MD rate constants were estimated assuming a first order kinetic law and fitting the long time behavior of \( \ln([N_0−N]/[N_0]) \) with a straight line. Here, \( N_0 \) is the total number of trajectories and \( N \) is the number of trajectories dissociated at time \( t \). This approach differs somewhat from the procedure used by Weerasinghe and Amar,\(^\text{13} \) who used the last negative minimum of the radial momentum for the dissociating atom to define the dissociation time. It also introduces some arbitrariness in the results, which are independent of the separatrix location only when the latter is placed in a region where the interaction potential has completely died off. Preliminary test runs, however, provided evidence that the rate constants are fairly insensitive to the critical dissociation distance, provided the residual potential is small. Thus, 4r was found to represent an adequate compromise between accuracy and computational cost for all values of \( n \), \( E \), and \( J \). To test for the suitability of the first order kinetic law, trajectories have been also analyzed plotting lifetime distributions. Generally speaking, lifetimes were found to follow the single exponential distribution predicted by the Rice-Ramsperger-Kassel-Marcus (RRKM) theory\(^\text{30} \) within the statistical precision of our simulations, the only exception being represented by clusters with high internal energy. Even in these cases, however, only minor deviations were noticed as will be discussed in the following.

Figure 2 (panel a) shows the behavior of \( k_n^d(E,J) \) as a function of \( n \), \( E \), and \( J \) obtained using MD simulations. Panel b in Fig. 2 provides a graphical representation for the probability distribution function \( p(J) \) of \( J \) at the energies employed in the MD simulations. The values of energy used to investigate the \( J \)-dependency of \( k_n^d(E,J) \) (Fig. 2) were chosen in order to explore situations of medium and high energy content for the LJ clusters; in all cases, the species are liquidlike. For all cluster sizes, only small changes in \( k_n^d(E,J) \) as a function of \( J \) are seen. The nature of these changes appear to be nonsystematic and probably due to mild sampling issues. The only deviation from this rule is represented by the case of LJ\(_{19} \) at \( E=−0.016 \) hartree, for which \( k_n^d(E,J) \) increases, roughly, by 20% for \( J>200 \) a.u. Overall, the results shown in Fig. 2 support the previous observation on LJ\(_{12,14} \) (Ref. 13) and Al\(_6 \) (Ref. 18) indicating a weak \( J \)-dependency of the dissociation rate. Bearing in mind the wide range of difference between the structure of the parent and daughter clusters explored in this work and Refs. 13 and 18, we interpret our numerical results (Fig. 2) as suggesting that it may be legitimate to neglect the dependency of \( k_n^d(E,J) \) on \( J \) for atomic aggregates of similar size. As a direct consequence of this assumption, additionally the dependency of \( k_n^d(E→E',J→J') \) on the angular momentum \( J' \) of the daughter cluster could be neglected while considering an evaporation cascade. This is easily understood: given the weak dependency on the angular momentum of the dissociation rate, there is no obligation to keep track of the amount of energy injected in the cluster rotational motion to describe a subsequent dissociation step. In this way, one is also relieved from the burden of estimating the probability of finding the daughter cluster with total angular momentum \( J' \) given an initial total angular momentum \( J \) for the parent (see, however, Ref. 31 for an alternative approach that explicitly takes \( J' \) into account). This approximation is of course reasonable unless a substantial amount of rotational heating/cooling takes place during the dissociation processes, a possibility that, however, appears unlikely.\(^\text{15} \)

In retrospective, the weak dependency of \( k_n^d \) on \( J \) highlighted by the MD results could have been easily foreseen from simple statistical consideration. Assuming equipartition of the internal energy between modes, one quickly reaches the conclusion that only a small fraction (roughly 3/\([2(3n−6)+3]\)) of the total energy would be into the rotational modes. This result, in turn, suggests that the vast majority of the energy needed during the dissociation process is made available by the vibrational modes, so that keeping track of the cluster rotational energy may generally not be of prime importance. In this way, a substantial simplification of the calculations and a reduction in the associated computational cost is introduced and we shall therefore assume in the rest
of this work that only a negligible dependency on the total angular momentum of the dissociation rates is present and focus only on the $\mu$-ensemble.

**B. Comparison between $\mu$-vTST and MD dissociation rates**

Bearing in mind the results discussed in the previous paragraphs, it appears therefore useful to benchmark the accuracy afforded by TST in predicting $k^d(E)$ for LJ clusters. Perhaps surprisingly, the only comparison between exact and statistical rates present in literature for these systems was carried out for PST on LJ$_{12-14}$ whereas no tests are available for the microcanonical version of TST provided by Eq. (6) to the best of our knowledge. In this situation, a more general test employing a set of atomic clusters featuring largely different structures appears as a worthwhile exercise as it could support more general conclusions.

To partially fill this gap, statistical and MD dissociation rate constants for LJ$_8$, LJ$_{14}$, and LJ$_{19}$ have been computed over a wider range of energies than explored in Sec. III A. MD simulations were run and analyzed with a protocol identical to the one used to investigate the $J$ dependency of $k^d(E,J)$. As discussed in Sec. II, a microcanonical adaptation of the procedure described in Ref. 27 was used to compute TST rates. This employs US to guide the configurational sampling close to the possible TS region and a discretization error-free estimator for the Dirac delta. In the TST calculations, a variable number of US windows was used as a function of the cluster size (2 for LJ$_8$, 3 for LJ$_{14}$, and 5 for LJ$_{19}$). To reduce the likelihood of quasiergodic behavior for simulations at low energy, a microcanonical replica-exchange MMC approach was implemented according to the rules discussed in Ref. 33. In this approach, all MMC calculations needed to span the energy interval of interest for a given cluster are run concurrently, exchanging configurations between energetically close simulations with an exchange probability that conserves the microcanonical distribution at both energies. This allows configurations unlikely to be sampled by low energy simulations to “percolate down” from high energy ones, facilitating the sampling of region in configuration space separated by energy barriers. The set of energy values employed in the microcanonical MMC runs were chosen in order to obtain an exchange rate of, at least, 20%–30% between neighbor energy values during preliminary test simulations; $10^6$ configurations per energy were sampled during each US simulation. The value of $k^d(E)$ [Eq. (6)] was computed as a function of $r_C$ over a grid of equispaced points separated by 1 bohr. Five to seven simulations were used to estimate these values obtaining a statistical accuracy of roughly 10%. The variational nature of TST rate constants was exploited selecting the location of the separatrix ($r_C$) over the chosen grid as the one that minimizes the value of $k^d(E)$. The simulation protocol employed for the TST calculations is fairly efficient and allows one to extend the range of energies substantially below the one accessible by MD thanks to its lower computational cost. In the energy range investigated, the clusters undergo a phase change from solidlike to liquidlike upon increasing the internal energy.

### TABLE I. Monomer dissociation rates for LJ$_8$ as a function of the internal energy $E$ computed using MD and TST simulations.

<table>
<thead>
<tr>
<th>$E$ (hartree)</th>
<th>$k^d_{\text{MD}}$ (ps$^{-1}$)</th>
<th>$k^d_{\text{TST}}$ (ps$^{-1}$)</th>
<th>$k^d_{\text{MD}}(E)/k^d_{\text{TST}}(E)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-0.005$</td>
<td>$0.00032$</td>
<td>$0.00032$</td>
<td>1.00</td>
</tr>
<tr>
<td>$-0.00475$</td>
<td>$0.00013$</td>
<td>$0.00016$</td>
<td>0.81</td>
</tr>
<tr>
<td>$-0.0045$</td>
<td>$0.00041$</td>
<td>$0.00072$</td>
<td>0.57</td>
</tr>
<tr>
<td>$-0.00425$</td>
<td>$0.0021$</td>
<td>$0.0022$</td>
<td>0.50</td>
</tr>
<tr>
<td>$-0.00405$</td>
<td>$0.0040$</td>
<td>$0.0040$</td>
<td>0.6</td>
</tr>
<tr>
<td>$-0.0035$</td>
<td>$0.0081$</td>
<td>$0.013$</td>
<td>0.62</td>
</tr>
<tr>
<td>$-0.003$</td>
<td>$0.019$</td>
<td>$0.021$</td>
<td>0.91</td>
</tr>
<tr>
<td>$-0.0025$</td>
<td>$0.045$</td>
<td>$0.033$</td>
<td>1.37</td>
</tr>
</tbody>
</table>

The results of the MD and TST simulations are reported in Tables I–III and shown in Fig. 3. Tables I–III also report the recrossing factor $k^d_{\text{MD}}(E)/k^d_{\text{TST}}(E)$. From these data, one notices a good agreement between variational TST and MD rates, the two sets of data differing at most by a factor of 2 over the energy range accessible by MD simulations. As usual, TST deviates the most from MD at high energy, whereas low energy TST dissociation constants are off by less than 30%. To highlight the better computational performances of the TST based approach, in Table III we have also included rate constants computed in a range of $E$ substantially lower than the one accessible by trajectory simulations for LJ$_{19}$. These additional results show that TST is, indeed, capable of providing an estimate for rates spanning roughly 20 orders of magnitude. As for the relative performances versus cluster size, the largest differences between TST and MD rates are seen for LJ$_8$ and LJ$_{19}$; we suspect this finding to be related to a less spherical structure for LJ$_7$ and LJ$_{18}$ than for LJ$_{13}$ and our choice of a spherical separatrix.

A more detailed analysis of the trajectory results indicated the presence of moderate nonstatistical effects for high energy species, with a slightly faster decay of $\ln([N_0 − N_j]/N_0)$ at short time than at longer time (Fig. 4). To test for quasiergodic behavior, the slope of $\ln([N_0 − N_j]/N_0)$ at $t=0$ was also computed. The latter was found to differ from

### TABLE II. Monomer dissociation rates for LJ$_{14}$ as a function of the internal energy $E$ computed using MD and TST simulations.

<table>
<thead>
<tr>
<th>$E$ (hartree)</th>
<th>$k^d_{\text{MD}}$ (ps$^{-1}$)</th>
<th>$k^d_{\text{TST}}$ (ps$^{-1}$)</th>
<th>$k^d_{\text{MD}}(E)/k^d_{\text{TST}}(E)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-0.011$</td>
<td>$0.00137$</td>
<td>$0.00137$</td>
<td>1.00</td>
</tr>
<tr>
<td>$-0.0105$</td>
<td>$0.0014$</td>
<td>$0.0021$</td>
<td>0.67</td>
</tr>
<tr>
<td>$-0.0100$</td>
<td>$0.0039$</td>
<td>$0.0039$</td>
<td>0.67</td>
</tr>
<tr>
<td>$-0.0095$</td>
<td>$0.0062$</td>
<td>$0.0062$</td>
<td>1.23</td>
</tr>
<tr>
<td>$-0.0085$</td>
<td>$0.015$</td>
<td>$0.015$</td>
<td>0.87</td>
</tr>
<tr>
<td>$-0.0080$</td>
<td>$0.023$</td>
<td>$0.023$</td>
<td>1.00</td>
</tr>
<tr>
<td>$-0.0075$</td>
<td>$0.028$</td>
<td>$0.028$</td>
<td>1.00</td>
</tr>
<tr>
<td>$-0.0070$</td>
<td>$0.039$</td>
<td>$0.039$</td>
<td>1.00</td>
</tr>
<tr>
<td>$-0.0065$</td>
<td>$0.046$</td>
<td>$0.046$</td>
<td>1.00</td>
</tr>
</tbody>
</table>
A table and some text follow:

**TABLE III.** Monomer dissociation rates for LJ₉ as a function of the internal energy E computed using MD and TST simulations. The adiabatic dissociation energy for a monomer is 0.002349 973 hartree. To highlight the effectiveness of the TST approach, rate constant values at energies substantially below the ones accessible by MD simulations have also been included. Statistical errors are of the order of 1% and 10% of the quoted results for MD and TST, respectively.

<table>
<thead>
<tr>
<th>E (hartree)</th>
<th>k₉MD(E) (ps⁻¹)</th>
<th>k₉TST(E) (ps⁻¹)</th>
<th>k₉MD(E)/k₉TST(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−0.024</td>
<td>7.7 × 10⁻³⁸</td>
<td>2.4 × 10⁻¹³</td>
<td></td>
</tr>
<tr>
<td>−0.023</td>
<td>4.6 × 10⁻⁹</td>
<td>7.3 × 10⁻¹⁷</td>
<td></td>
</tr>
<tr>
<td>−0.022</td>
<td>0.000 995</td>
<td>0.000 346</td>
<td>1.64</td>
</tr>
<tr>
<td>−0.021</td>
<td>0.000 346</td>
<td>0.000 346</td>
<td>0.95</td>
</tr>
<tr>
<td>−0.020</td>
<td>0.000 346</td>
<td>0.000 346</td>
<td>0.95</td>
</tr>
<tr>
<td>−0.019</td>
<td>0.000 346</td>
<td>0.000 346</td>
<td>0.95</td>
</tr>
<tr>
<td>−0.018</td>
<td>0.000 346</td>
<td>0.000 346</td>
<td>0.95</td>
</tr>
<tr>
<td>−0.017</td>
<td>0.000 346</td>
<td>0.000 346</td>
<td>0.95</td>
</tr>
<tr>
<td>−0.016</td>
<td>0.000 346</td>
<td>0.000 346</td>
<td>0.95</td>
</tr>
<tr>
<td>−0.015</td>
<td>0.000 346</td>
<td>0.000 346</td>
<td>0.95</td>
</tr>
<tr>
<td>−0.014</td>
<td>0.000 346</td>
<td>0.000 346</td>
<td>0.95</td>
</tr>
<tr>
<td>−0.013</td>
<td>0.000 346</td>
<td>0.000 346</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Apart from exploring the possibility of nonstatistical behavior during cluster dissociation, the possible impact of anharmonicity on kₙ(E) was assessed by fitting low energy TST rates for all clusters with the RRK expression log[kₙ(E)] = log(π)+(s−1)log[(E−E₀)/E]. Here, E is the internal energy of the cluster and E₀ is its evaporation energy (i.e., the energy necessary to detach a monomer from the global minimum of Ljn, producing the global minimum of LJn−1). Overall, the RRK expression was found to performed quite well, even though the fitting process produced larger s values than suggested by counting the vibrational degrees of freedom (s₉RRK=3×n−6) for LJ₈ and LJ₁₄. Specifically, s was found to be 22, 44, and 50 for n=8, 14, and 19, respectively. According to Song and Hase, an s value larger than the number of modes is likely to be due to anharmonic effects, which allow the sum of states for the TS (N₉(E)) to grow more rapidly than the reactant density of states (ρ(E)). This seems to be the case for both LJ₈ and LJ₁₄ that are liquidlike in the range of energies used to extract s. Differently, LJ₁₉ is solid-like.
like in the range of $E$ employed in the fitting procedure and the obtained $s$ value, only slightly lower than the theoretical $s_{RRK}$, seems to suggest that the cluster is behaving in reasonable accord with the harmonic approximation used to derive the RRK rate expression. An additional deviation from the classical RRK behavior might be present in barrierless dissociations due to a contraction of the TS distance upon increasing the internal energy. This contraction may affect both the effective value of the dissociation energy and the absolute value of $v$ (for harmonic modes this term is given by $v=\Pi_{i=1}^{N}v_i/\Pi_{i=1}^{N}v_i^2$ where $v_i$ and $v_i^2$ are the harmonic frequencies of the reactant and TS, respectively). However, we found only small changes (1 bohr) in the locations of the TS as a function of $E$, suggesting a minor role for this effect.

To conclude this section, it appears necessary to comment on the total cost of both MD and statistical TST simulations, providing evidence for the better efficiency and reduced computational effort suggested earlier for MMC-TST calculations. To do so, let us focus on the largest and most demanding cluster studied, namely, LJ$_{19}$. For this, obtaining low energy MD dissociation rates required a minimum of 2500 trajectories and roughly 55 min per energy on an Intel 3.0 GHz processor. In those conditions, we found that only a small fraction (e.g., 60 over 2500) of trajectories are reactive and that the total computational time decreases by up to a factor of 3 due to faster trajectory dissociation at higher energy. To estimate TST rates, five US windows were used to force the MMC simulation to visit the relevant range of $r_{\text{IRC}}$ (16–40 bohr), each of which sampled $10^6$ configurations at 12 different energies and required roughly 20 min. Six additional simulations of similar length were successively employed to estimate $\langle \delta(r_{\text{IRC}}-r_c) \rangle$, with a total cost of roughly 18 min per energy. As a consequence, TST allows a threefold decrease in computational time at the lowest energy still amenable to MD simulations.

### C. KER distributions

From the results discussed in Sec. III B, we conclude that the version of TST given by Eq. (6) may indeed be capable of providing accurate dissociation rate constants for LJ$_n$ over a wide range of energies and a substantial saving in computer time for processes at low energy. It would seem therefore possible to rely on MD simulations only for the most difficult cases or at high values of $E$.

In our view, there is an additional and more compelling reason to employ TST in modeling the dissociation of atomic and molecular clusters, a reason that has been partially introduced in the work by Calvo and Parneix. As discussed in Sec. I, modeling a cluster dissociation cascade by means of a set of MEs necessitates use of either $P_j(E, \epsilon_r)$ (the distribution of $E_r$ as a function of $E$ and $J$) or $P_j(E, \epsilon)$ (the distribution of $E$, as a function of $E$ if the $J$-dependency is neglected). Unfortunately, obtaining a precise estimate for these distributions with MD is more demanding than the calculation of $P^D_{\text{IRC}}(E)$. For instance, we found that a minimum of $10^5$ dissociated trajectories were needed to obtain a reasonably precise $P_r(E, \epsilon_r)$ for LJ$_8$. From these data and the small fraction of low energy dissociation events witnessed for LJ$_{19}$ (roughly 2.5%), it is possible to estimate that at least 153 h would be needed to obtain a low energy KER distribution for LJ$_{19}$.

The difficulty related to the large number of dissociated trajectories needed for the construction of $P_r(E, \epsilon_r)$ could, in principle, be circumvented using TST. In fact, Calvo and Parneix already showed that accurate KER distributions can be obtained using PST at a small fraction of the computational cost required by MD (Ref. 15) provided that $\Omega(E)$ and the correct integration boundaries in energy and momentum space are available. As mentioned previously, Eq. (8) circumvents the necessity for an accurate estimate of $\Omega(E)$ and it is expected to feature a similarly reduced computational cost. However, the performance of Eq. (8) in predicting $P_r(E, \epsilon_r)$ need to be properly assessed, the results of this task being described in the following paragraphs.

To produce a comparison for $P^\text{MD}_{\text{IRC}}(E, \epsilon_r)$ (Eq. (8)), at least $10^5$ dissociated MD trajectories have been collected for each cluster size and value of internal energy investigated. Trajectory simulations have been carried out following protocols discussed in Secs. III A and III B. More specifically, trajectories were dubbed as dissociated at $r_{\text{IRC}}=4\sigma$ and analyzed to extract both $E_r$ and $E_r$ with the scheme proposed in Sec. II for the analysis of the TST simulations. Histograms for $P^\text{TST}_{\text{IRC}}(E, \epsilon_r)$ were obtained collecting samples composed of $10^4$ independent configurations distributed according to the $\mu$-TS ensemble by means of MMC simulations. In the latter, Jacobi coordinates were used instead of the Cartesian ones to maintain the dissociating atom on the separatrix. For each configuration $\mathbf{q}$ extracted from the MMC runs, 20 independent momentum samples were generated as suggested earlier, producing a total of $2 \times 10^5$ independent momentum samples for energy and cluster size.

Figure 5 shows the KER distributions for the three cluster sizes and selected values of the internal energy. Overall, the results presented in Fig. 5 indicate a good agreement between MD and TST distributions, especially at low internal energy. At higher internal energies, the agreement slightly deteriorates for low values of $\epsilon_r$, whereas the behavior at high $\epsilon_r$ is reasonably well reproduced (panels a and b). More specifically, the TST distributions suggest a higher probability for low $\epsilon_r$ values than the MD counterparts. A similar behavior (not shown) was also found for the distribution of $E_r$.

At the moment, we find it difficult to completely rationalize the difference between MD and TST results. This may be due, for instance, to nonstatistical effects, i.e., to nonstatistical energy distributions in the products, which may lead to a more substantial accumulation of energy either along the reaction coordinate or in the rotational motion of the fragment cluster. Another possible source of difference comes from the fact that different separatrix locations are used in MD and TST simulations, the optimized separatrix radius $r_c$ in TST always being shorter than the fixed distance $r_C=4\sigma$ used for MD trajectories. Because a phase space point is implicitly labeled as “reactive” in Eq. (7) based only on a positive value of the projection of its velocity along the reaction coordinate, some residual interaction between the two fragments may still be present due to the shorter $r_C$.
IV. CONCLUSIONS

This work reports an investigation exploring the possibility of theoretical and computational simplifications that could be introduced in studying the quantitative details of dissociating atomic clusters. The underlying motivation behind this study is the desire of extending DNT to the microcanonical ensemble (or the J-resolved microcanonical ensemble), the latter being a more natural framework to deal with gas phase activated processes such as collision-induced dissociation.

The first simplification comes from noticing that \( k^b_n(E,J) \) is substantially independent of \( J \), the total angular momentum of the activated aggregate, for the range of cluster sizes and energies explored in this work. As a net consequence of this, one would therefore be allowed to focus only on the energy dependency of \( k^b_n \) with a substantial reduction in both the complexity and cost of the calculations. However, it is important to stress that the reason for introducing this simplification is only related to the total cost of computing dissociation rates and not to an intrinsic limitation of TST in dealing with nonzero angular momentum. In fact, it would be straightforward to extend it using the procedure suggested in Ref. 31.

When modeling parallel dissociation/condensation processes, the weak sensitivity of \( k^b_n(E,J) \) with respect to \( J \) may allow one to introduce another simplification in the ME set, namely the possibility of neglecting the dependency on \( J \) of the condensation rate constant \( k^c_{n-1}(E' \rightarrow E,J' \rightarrow J) \), \( L' \) indicating the orbital angular momentum of the colliding system. Similarly to that discussed previously, this simplification would rely on the fact that the dissociation lifetime of \( M_n \) only weakly depends on \( J \), but it would be fully justified only if \( k^c_{n-1} \) was also found to be largely independent of \( J' \), an issue currently under investigation in our laboratory.

As for the dependency of \( k^c_{n-1}(E' \rightarrow E,J' \rightarrow J) \) on \( L' \), indirect evidence for a simple behavior of \( k' \) with respect to \( L' \) was provided by Napari et al.,\(^{37}\) who carried out MD simulations to study the monomer capture probability by cold LJ clusters as a function of the collision parameter \( b \). The capture probability (and the lifetime \( \tau \) of the formed cluster) was found to be practically insensitive to \( b \), hence to \( L' \), provided \( b \) was within the cluster radius. At larger collision parameters, the capture probability becomes almost negligible suggesting the possibility of modeling the condensation process as a function of \( L' \) using a steplike function for the capture probability. Notice, however, that Georgievskii and Klippenstein\(^{38}\) reported improvements in the accuracy of long range TST when the full \( J \)-vTST version is used. Needless to say, a more accurate investigation of this issue for atomic clusters would be worthwhile but it is outside the scope of this work.

Evidence has been also provided for a good performance of TST with respect to MD in predicting the dissociation rate constant as a function of the aggregate internal energy \( E \). Bearing in mind that usually TST performs rather well at low energy, i.e., when MD becomes inefficient, this finding suggests that statistical \( k^b_n(E) \)'s obtained with Eq. (6) could be used at all but the highest values of internal energy with a

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**FIG. 5.** (Color online) MD and TST KER distribution for LJ\(_n\) at different values of \( E \). (a) \( n=14 \); (b) \( n=8 \); (c) \( n=19 \). The distributions have been normalized so that \( \int P(E,E_n)\,dE_n=1 \). Energy in hartree.
substantial saving in computational time. Importantly, the version of TST used in this work [see Eq. (6)] lends itself to be merged with a microcanonical extension of replica exchange algorithm, thus improving the exploration of the configuration space, and fully accounts for the anharmonic behavior of \( L_j \). As previously shown by Peslherbe and Hase\(^{18}\) for PTS, the correct treatment of anharmonicity is an indispensable ingredient for an accurate prediction of dissociation rates for fluxional species.

The knowledge of \( k^0_n(E) \) over a wide range of energies would, in principle, allow one to also obtain \( k^0_n(T) \) by convolving the normalized Boltzmann distribution \( P^0_n(T,E) dE = \Omega(E) e^{-E/k_B T} dE / \int \Omega(E) e^{-E/k_B T} dE \) for \( L_j \) at the chosen temperature \( T \). According to this prescription, one also needs to know \( \Omega(E) \), the system density of states, in order to obtain \( k^0_n(T) \). Unfortunately, the accurate calculation of \( \Omega(E) \) is far from trivial (see e.g., Ref. 20 for a discussion), explicitly avoided by the method described in Sec. II, and it is therefore considered outside the scope of this work. Besides, we suspect that the direct calculation of \( k^0_n(T) \) using, for instance, the approach described in Ref. 27 would be as efficient, if not more, than obtaining \( \Omega(E) \) and, subsequently, computing the convolution integral.

Finally, the performance of a TST-based approach [Eq. (8)] to predict KER distributions has been tested against MD results and shown to provide quantitative accuracy at low internal energies. At higher energies, the agreement slightly deteriorates, probably due to nonstatistical behavior or to the different method used to label a phase space point as reactive. Nevertheless, our approach appears to provide, overall, a robust and computationally efficient tool for the calculation of this important quantity.

Armed with the simplifications discussed above, TST could therefore become a powerful tool to study the atomistic details of cluster dissociation cascades. Needless to say, several issues still need to be addressed before it becomes of general applicability. In this respect, it is important to point out that better choices for the separatriz (e.g., nonspherical or momentum dependent) may further improve its accuracy and that further algorithmic development is likely to reduce the computational cost with respect to trajectory simulations even more. Work in these directions is currently carried out in our laboratory.

With the long term goal of simulating homogeneous vapor-liquid condensation, one should also be concerned with the performance of TST in predicting the capture of a monomer by an already formed aggregate and the subsequent dissociation or de-energization process that may be induced by a postcapture collision with another body. The latter processes may, in principle, be modeled also in the TST framework\(^ {30}\) provided that the lifetime of the energized cluster is long enough to allow for intrasystem energy redistribution. Evidence for well separated time scales between energy redistribution and dissociation has been provided by Napari and Vehkämäki,\(^ {40}\) who highlighted the short time required for energy redistribution (maximum 30 ps) and the small role played by unrelaxed clusters. Given the fact that the \( k^0_n(E) \) values reported in this work suggest a cluster lifetime at least an order of magnitude longer, it would be interesting to explore the overall accuracy of a two step TST approach to the condensation/dissociation process.

**ACKNOWLEDGMENTS**

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