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Rotation/translation interplay in the recoil statistics of cluster evaporation

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Abstract. A new statistical model has been developed in the framework of Phase Space Theory to describe the evaporation process of non-rotating clusters. The novelty of the theoretical approach resides in its ability to easily separate the total kinetic energy released in an evaporation process into the rotational and translational contributions. This new model has been tested by comparing its predictions with the results of Molecular Dynamics (MD) simulations for the unimolecular evaporation of two types of van der Waals clusters: the aniline-(argon)$_n$ molecular clusters and the neat argon Ar$_n$ clusters.

PACS. 36.40.Ei Phase transition in clusters – 82.20.Db Statistical theories (including transition state)

1 Introduction

During the last decade many experimental and theoretical studies, devoted to the physics and chemistry of clusters, have considerably improved our understanding of their intimate dynamical behaviour. Some new and fascinating concepts, such as the solid-liquid like transition and the dynamical coexistence in finite size systems, have been proposed [1–4]. These *phase transitions* in such small systems, initially characterized from changes and fluctuations of structural parameters, have been clearly analyzed from a thermodynamical point of view first by Labastie and Whetten [5] in pure Ar$_n$ clusters. They have been recently observed experimentally in the case of Na$_n$ metal clusters [6]. More generally, the relationship between structure, dynamics and thermodynamics in homogeneous or inhomogeneous clusters has been explored [7].

From the theoretical point of view, most of the effort has been focussed on the study of van der Waals (vdW) clusters since simple and reliable interaction potentials can be used. In these vdW systems, interesting experimental informations have been collected on the evolution of the chemical and physical properties of a molecular chromophore as a function of the number of atomic species which are bound around it. As an example, the aromatic-rare gas systems have been extensively studied [8–12]. Unfortunately, no experimental unambiguous proof of phase transition has been found yet in vdW clusters.

The direct connection between phase transition and the microcanonical density of states has stimulated Amar and Weerasinghe [13] to analyse the evaporation process from both molecular dynamics (MD) simulations and phase space theory (PST). In this statistical approach, the evaporation rate and the average kinetic energy release can be directly calculated from the densities of states of the reactant and of the product clusters. It has been clearly demonstrated, both in their work [13] and in a subsequent work by ourselves [14], that the phase transition in the product clusters has an influence on the energetics and on the dynamics of the unimolecular process. It could open the route to new experiments in which the kinetic energy release will be measured as a function of the internal energy deposited in the parent cluster.

A direct comparison between experimental results and theoretical predictions could then be possible if the mean *rotational* energy of the sub-cluster can be evaluated. Indeed, in a typical experiment, only the *translational* kinetic energy of the fragments will be measured. Unfortunately, in the PST formalism, only the *total* kinetic energy is calculated. No information on the partition of the release energy between the two kinds of external degrees of freedom (translation and rotation) in the exit channel is available. In this paper, we propose as an extension of the PST formalism a theoretical approach which enables to fully characterize this energy partition in the case of non-rotating parent clusters, through the rotational and translational energy distributions functions.

The main features of this approach, including the necessary approximations and its predictive character, have been tested by using as a benchmark the results of MD simulations, performed separately on two well-studied vdW systems: the aniline-(argon)$_n$ clusters and the neat argon Ar$_n$ clusters. However, a major interest of such a statistical model, as opposed to MD simulations, is its faculty to match the characteristic lifetime of evaporating clusters in actual experiments, as it has previously been stressed [14].

This paper is divided into two main sections. In Section 2, the new statistical model to calculate the translational and rotational contributions in the evaporation

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process is presented. In Section 3, a comparison is made between the results obtained from this statistical model and from MD simulations in the case of the evaporation of aniline-Ar$_n$ clusters and of neat Ar$_n$ clusters.

2 The new statistical model

2.1 Phase space theory frame

The statistical approach known as PST has been first developed for reactive collisions by Light [15,16] and then used for describing the unimolecular processes in highly energetised molecules by Klots [17]. In warm van der Waals clusters, this method has shown its ability to give reliable values of the mean kinetic energy release (KER) and of the unimolecular evaporation rate. In particular the evolution of the evaporation rate and of the KER as a function of the internal energy of the parent cluster was found in good agreement with MD results in the case of Ar$_n$ clusters [13] and of aniline-Ar$_n$ clusters [14]. In the PST formalism for evaporation, the transition state is considered as the ensemble of the product cluster and the separated atom (loose state theory) and the key function is the differential rate $R(\epsilon;E)$ given by:

$$R(\epsilon;E) = \frac{1}{h}\frac{\omega^{(\mathrm{TS})}(E-E_0-\epsilon)}{\omega^{(\mathrm{r})}(E)} \tag{1}$$

h is the Planck's constant. E_0 corresponds to the energy difference between the transition state and the reactant. ϵ is the total kinetic energy released in the reaction. $\omega^{(\mathrm{r})}$ and $\omega^{(\mathrm{TS})}$ are respectively the densities of states associated to the reactant and to the transition state.

Separating the vibrational coordinates from the external degrees of freedom at the transition state, the differential rate $R(\epsilon;E)$ can be rewritten as:

$$R(\epsilon;E) = \frac{1}{h}\frac{\omega_{\mathrm{rt}}(j=0,E)\,\omega_{\mathrm{v}}^{(\mathrm{p})}(E-E_0-\epsilon)}{\omega^{(\mathrm{r})}(E)}\cdot \tag{2}$$

In this last expression $\omega_{\mathrm{rt}}(j=0,E)$ corresponds to the recoil translational and rotational density of states and $\omega_{\mathrm{v}}^{(\mathrm{p})}(E-E_0-\epsilon)$ corresponds to the vibrational density of states of the product cluster. $j=0$ is a recall that the parent cluster is not rotating. This expression can be used with benefit to calculate the evaporation rate constant:

$$k_{\mathrm{e}}(E) = \int_0^{E-E_0} R(\epsilon;E)\,\mathrm{d}\epsilon \tag{3}$$

and the average KER:

$$\langle\epsilon\rangle = \int_0^{E-E_0} \epsilon R(\epsilon;E)\,\mathrm{d}\epsilon \bigg/ \int_0^{E-E_0} R(\epsilon;E)\,\mathrm{d}\epsilon \tag{4}$$

if some approximate behaviour of $\omega_{\mathrm{rt}}(j=0,E)$ is taken into account.

We have shown in a previous article [14] that this "external" density of states is proportional to the total KER ϵ to a good approximation. Indeed, following the work of Chesnavich and Bowers [18], it can be shown that $\omega_{\mathrm{rt}}(j=0,E)$ is proportional to $J^2_{\max}$, $J_{\max}$ being the maximum value of the angular momentum for the product cluster. This proportionality has been obtained in the case of a non-rotating reactant cluster ($j=0$) and by considering the cluster as a sphere-atom system and by applying the constraints linked to the energy and angular momentum conservation in the separation process.

On the other hand, $J^2_{\max}$ can be approximately considered as proportional to the total KER ϵ. We have shown [14] that the maximum value of the sub-cluster rotational energy $\epsilon_{\mathrm{rot}}^{(\max)}$ is related to the maximum value $R_{\max}$ of the interfragment distance by the following expression:

$$\epsilon_{\mathrm{rot}}^{(\max)} = \frac{1}{1+\dfrac{\mu}{2\overline{B}M^2R^2_{\max}}}\,\epsilon \tag{5}$$

in which μ is the reduced mass of the (sub-cluster–atom) system, and $\overline{B}$ corresponds to the mean rotational constant for the sub-cluster.

This last expression can be now simplified by expressing the mean rotational constant $\overline{B}$ of the product cluster as $\overline{B} = [2\ (n-1)M_{\mathrm{Ar}}R^2_{\mathrm{sc}}]^{-1}$. This relation can be considered as a definition of R_{sc}, which can be viewed as a typical "inertial" size of the sub-cluster. Typical values of R_{sc} can be evaluated from the calculation of the structure of the most stable isomer. As $\mu/M_{\mathrm{Ar}} = M_{n-1}/M_n$ and by calling $\alpha_n = R_{\max}/R_{\mathrm{sc}}$, equation (5) can be rewritten as:

$$\epsilon_{\mathrm{rot}}^{(\max)} = \frac{1}{1+\dfrac{(n-1)M_{n-1}}{\alpha_n^2 M_n}}\epsilon = \gamma_n\epsilon \tag{6}$$

by introducing

$$\gamma_n = \frac{1}{1+\dfrac{(n-1)M_{n-1}}{\alpha_n^2 M_n}}$$

which can be viewed as a purely inertial factor.

We have to note that this linearity is not rigorous. In fact, the relation between $J_{\max}$ and ϵ should be extracted from the relationship:

$$\epsilon_{\mathrm{rot}}^{(\max)} = \epsilon - \epsilon^* \tag{7}$$

in which ϵ^* corresponds to the height of the centrifugal barrier. Our assumption of linearity is then directly linked to the proportionality of ϵ^* with ϵ. The direct consequence of the linearity between $\epsilon_{\mathrm{rot}}^{(\max)}$ (and consequently $J^2_{\max}$) and ϵ is that the evaporation rate constant $k_{\mathrm{e}}(E)$ and the mean total kinetic energy release $\langle\epsilon\rangle$ can be extracted from a simple integration on only one variable, namely ϵ, by:

$$k_{\mathrm{e}}(E) \propto \frac{\int_0^{E-E_0}\epsilon\,\omega_{\mathrm{v}}^{(\mathrm{p})}(E-E_0-\epsilon)\,\mathrm{d}\epsilon}{\omega_{\mathrm{v}}^{(\mathrm{r})}(E)} \tag{8}$$

and

$$\langle\epsilon\rangle = \frac{\int_0^{E-E_0} \epsilon^2 \omega_{\mathrm{v}}^{(\mathrm{p})}(E-E_0-\epsilon)\,\mathrm{d}\epsilon}{\int_0^{E-E_0} \epsilon\omega_{\mathrm{v}}^{(\mathrm{p})}(E-E_0-\epsilon)\,\mathrm{d}\epsilon}\cdot \tag{9}$$

However the application of such a PST formalism does not bring any information about the relative input of the released kinetic energy into the two contributions (rotational kinetic energy of the sub-cluster and relative translational kinetic energy). An alternative description to precisely obtain this information on the energy sharing in the exit channel is proposed in the next sub-section. Before describing it, we have to note that some other theoretical approaches exist to describe the unimolecular dissociation of an ensemble of atoms. The RRK theory [19,20] is naturally one of the most popular in particular due to the simple analytic expressions obtained from this approach. Marcus [21] has proposed an evolution of this model by using the concept of transition state [22]. Another interesting model has been proposed more recently by Engelking [23]. In fact the predictions of this last model can be found from the present PST formalism by using harmonic density of states and by assuming the linearity of $J^2_{\max}$ as a function of the total kinetic energy ϵ.

2.2 Explicit forms of the rotational and translational distributions

If we consider explicitly the density of states of the transition state as the product of the vibrational density of states of the $(n-1)$ cluster, the rotational density of states of the $(n-1)$ cluster and the translational part, the probability to obtain the rotational energy in the interval $[\epsilon_{\mathrm{rot}};\epsilon_{\mathrm{rot}}+\mathrm{d}\epsilon_{\mathrm{rot}}[$ and the relative translation energy in the interval $[\epsilon_{\mathrm{tr}};\epsilon_{\mathrm{tr}}+\mathrm{d}\epsilon_{\mathrm{tr}}[$ can be written as:

$$P(\epsilon_{\mathrm{rot}},\epsilon_{\mathrm{tr}};E) = f(\epsilon_{\mathrm{tr}},\epsilon_{\mathrm{rot}};E)\,\mathrm{d}\epsilon_{\mathrm{tr}}\,\mathrm{d}\epsilon_{\mathrm{rot}}$$
$$= \frac{\omega_{\mathrm{v}}^{(\mathrm{p})}(E-E_0-\epsilon_{\mathrm{tr}}-\epsilon_{\mathrm{rot}})\omega_{\mathrm{r}}(\epsilon_{\mathrm{rot}})\omega_{\mathrm{t}}(\epsilon_{\mathrm{tr}})\,\mathrm{d}\epsilon_{\mathrm{tr}}\,\mathrm{d}\epsilon_{\mathrm{rot}}}{\int\mathrm{d}\epsilon_{\mathrm{rot}}\int\omega_{\mathrm{v}}^{(\mathrm{p})}(E-E_0-\epsilon_{\mathrm{rot}}-\epsilon_{\mathrm{tr}})\omega_{\mathrm{r}}(\epsilon_{\mathrm{rot}})\omega_{\mathrm{t}}(\epsilon_{\mathrm{tr}})\,\mathrm{d}\epsilon_{\mathrm{tr}}}\cdot \tag{10}$$

In this expression the only vibrational density of states involved is that of the product $\omega_{\mathrm{v}}^{(\mathrm{p})}$ but the difficulty comes from the evaluation of the ω_{t} and ω_{r} functions. However we are going to show that analytic expressions can be easily derived.

If we consider the sub-cluster as spherical, the intermolecular potential depends only on the distance between the separating atom and the center of mass of the sub-cluster. Consequently the configuration of the transition state of the sub-cluster–atom system does not depend on the orientation of this system in space but only on the distance, R_{TS}. At a given $\mathbf{R}_{\mathrm{TS}}$, the rotational angular momentum of the sub-cluster $\mathbf{J}_{\mathrm{sc}}$ is in the plane perpendicular to $\mathbf{R}_{\mathrm{TS}}$, the latter connecting the evaporating atom and the center of mass of the sub-cluster. Indeed, as we only consider non-rotating parent clusters ($\mathbf{j}=\mathbf{0}$), $\mathbf{J}_{\mathrm{sc}}$ is colinear to the angular momentum of the evaporating atom $\mathbf{J}_e$ and then perpendicular to $\mathbf{R}_{\mathrm{TS}}$. Consequently we have to calculate the density of states of a 2D free rotor defined by a rotational constant $\overline{B}$. This density of rotational states will be proportional to $\epsilon_{\mathrm{rot}}^{g/2-1}$ where g (= 2 in this case) corresponds to the number of degrees of freedom. Thus we find a very simple result:

$$\omega_{\mathrm{r}}(\epsilon_{\mathrm{rot}}=\overline{B}\mathbf{J}^2_{\mathrm{sc}}) = \text{const.} \tag{11}$$

If we decompose now the linear momentum of the separating atom as the sum of its perpendicular and parallel to $\mathbf{R}_{\mathrm{TS}}$ components $\left(\mathbf{P}=\mathbf{P}^{(\perp)}+\mathbf{P}^{(\|)}\right)$ then $\epsilon_{\mathrm{tr}}=C+\mathbf{P}^{(\|)2}/2\mu$ in which $C=\mathbf{P}^{(\perp)2}/2\mu$. By taking $u=\epsilon_{\mathrm{tr}}-C$, we obtain $u=\mathbf{P}^{(\|)2}/2\mu$ and this expression can be viewed as the kinetic energy in a one dimensional problem for a particle whose mass is equal to μ. When $\mathbf{J}_{\mathrm{sc}}$ is given, the perpendicular component of $\mathbf{P}$ is fully determined and then C is a constant. Consequently the translational density of states is proportional to $u^{-1/2}$ and can be written as:

$$\omega_{\mathrm{t}}(\epsilon_{\mathrm{tr}}) \propto (\epsilon_{\mathrm{tr}}-K\epsilon_{\mathrm{rot}})^{-1/2} \tag{12}$$

in which the K constant is given for parent cluster of size n by:

$$K_n = \frac{(n-1)M_n}{M_{n-1}\beta_n^2} \tag{13}$$

where β_n is the distance ratio $R_{\mathrm{TS}}/R_{\mathrm{sc}}$.

As, in the case of vdW clusters, long range interactions are involved in the dissociation process, we can consider, in a first approximation, $R_{\mathrm{TS}} \gg R_{\mathrm{sc}}$ in which R_{sc} corresponds to the mean size of the sub-cluster. Then K_n becomes very small (β_n very large). If we neglect it *versus* ϵ_{tr}, equation (10) can then be rewritten as:

$$P(\epsilon_{\mathrm{rot}},\epsilon_{\mathrm{tr}};E) =$$
$$\frac{\omega_{\mathrm{v}}^{(\mathrm{p})}(E-E_0-\epsilon_{\mathrm{tr}}-\epsilon_{\mathrm{rot}})\epsilon_{\mathrm{tr}}^{-1/2}\,\mathrm{d}\epsilon_{\mathrm{tr}}\,\mathrm{d}\epsilon_{\mathrm{rot}}}{\int_0^{\epsilon_0}\mathrm{d}\epsilon_{\mathrm{rot}}\int_{\epsilon_1}^{\epsilon_2}\omega_{\mathrm{v}}^{(\mathrm{p})}(E-E_0-\epsilon_{\mathrm{tr}}-\epsilon_{\mathrm{rot}})\,\epsilon_{\mathrm{tr}}^{-1/2}\,\mathrm{d}\epsilon_{\mathrm{tr}}}\cdot \tag{14}$$

In this last expression, the values for the bounds ϵ_0, ϵ_1 and ϵ_2 are linked to energy conservation constraints induced by relations between translational and rotational contributions.

As ϵ is smaller than $(E-E_0)$ and by using equation (6), the maximum value taken by the rotational energy will be:

$$\epsilon_0 = \gamma_n(E-E_0). \tag{15}$$

From equation (6), we have $\epsilon_{\mathrm{rot}} \le \gamma_n(\epsilon_{\mathrm{rot}}+\epsilon_{\mathrm{tr}})$. Consequently we obtain that ϵ_{tr} is larger than $(1-\gamma_n)\epsilon_{\mathrm{rot}}/\gamma_n$. As ϵ_1 is defined as the minimum energy value taken by the translational kinetic energy for a given value of the rotational contribution ϵ_{rot}, it can be deduced:

$$\epsilon_1 = \frac{1-\gamma_n}{\gamma_n}\epsilon_{\mathrm{rot}}\cdot \tag{16}$$

Finally ϵ_2 is defined as the maximum value taken by the translational energy for a given value of the rotational energy ϵ_{rot}. As $\epsilon_{\mathrm{tr}} + \epsilon_{\mathrm{rot}} \leq E - E_0$, we directly find:

$$\epsilon_2 = E - E_0 - \epsilon_{\mathrm{rot}}. \tag{17}$$

The probability $P'(\epsilon_{\mathrm{rot}}; E)$ to obtain the rotational kinetic energy between ϵ_{rot} and $\epsilon_{\mathrm{rot}} + \mathrm{d}\epsilon_{\mathrm{rot}}$ at a given value of E can be calculated by summing over ϵ_{tr}:

$$P'(\epsilon_{\mathrm{rot}}; E) = g(\epsilon_{\mathrm{rot}}; E)\, \mathrm{d}\epsilon_{\mathrm{rot}} = \int_{\epsilon_1}^{\epsilon_2} f(\epsilon_{\mathrm{rot}}, \epsilon_{\mathrm{tr}}; E)\, \mathrm{d}\epsilon_{\mathrm{tr}}. \tag{18}$$

From this last equation, the mean rotational energy for a fixed value of the total energy E can be directly obtained by integrating over all the values of the rotational energy:

$$\langle \epsilon_{\mathrm{rot}} \rangle (E) = \int_0^{\epsilon_0} \epsilon_{\mathrm{rot}} g(\epsilon_{\mathrm{rot}}; E)\, \mathrm{d}\epsilon_{\mathrm{rot}}. \tag{19}$$

Following the same procedure, the probability $P''(\epsilon_{\mathrm{tr}}; E)$ to obtain the translational kinetic energy between ϵ_{tr} and $\epsilon_{\mathrm{tr}} + \mathrm{d}\epsilon_{\mathrm{tr}}$ at a given value of E can be calculated by summing over ϵ_{rot}:

$$P''(\epsilon_{\mathrm{tr}}; E) = h(\epsilon_{\mathrm{tr}}; E)\, \mathrm{d}\epsilon_{\mathrm{tr}} = \int_0^{\epsilon_3} f(\epsilon_{\mathrm{rot}}, \epsilon_{\mathrm{tr}}; E)\, \mathrm{d}\epsilon_{\mathrm{rot}} \tag{20}$$

with $\epsilon_3 = \min(\gamma_n \epsilon_{\mathrm{tr}}/(1-\gamma_n), E - E_0 - \epsilon_{\mathrm{tr}})$.

Finally the mean translational energy can be directly obtained from the $h(\epsilon_{\mathrm{tr}}; E)$ function by the following integral:

$$\langle \epsilon_{\mathrm{tr}} \rangle (E) = \int_0^{E-E_0} \epsilon_{\mathrm{tr}} h(\epsilon_{\mathrm{tr}}; E)\, \mathrm{d}\epsilon_{\mathrm{tr}}. \tag{21}$$

As a final remark it should be emphasized that explicit calculations of these mean values and distribution functions for ϵ_{rot} and ϵ_{tr} for a given system only need the knowledge of γ_n (which enters in the definition of ϵ_1, ϵ_3) or equivalently of α_n (see Eq. (7)) and of the vibrational density of states of the product cluster (to inject in Eq. (14)).

We will see in the test case studies presented in Section 3 how the inertial factor γ_n can be evaluated. The microcanonical density of states $\omega_{\mathrm{v}}^{(\mathrm{p})}(E)$ can be extracted to within a multiplicative factor from the multiple histogram method [5,24] after running canonical Nosé simulations [25] at different temperatures. Such simulations provide set of values for the probability $P_T(E)$ to obtain the energy E in the interval $[E; E+\Delta E[$. This probability is linked to the classical microcanonical density of states $\omega_{\mathrm{v}}^{(\mathrm{p})}(E)$ by:

$$P_T(E) = \frac{\omega_{\mathrm{v}}^{(\mathrm{p})}(E) \mathrm{e}^{-E/k_{\mathrm{B}}T} \Delta E}{Z(T)} \tag{22}$$

in which k_{B} is the Boltzmann constant and $Z(T)$ the partition function. And inversion of this formula gives $\omega_{\mathrm{v}}^{(\mathrm{p})}(E)$ to within an arbitrary multiplicative constant. We have to note that the calculation of the mean total kinetic energy (see Eq. (9)) and the mean rotational and translational kinetic energy release from the statistical model (see Eqs. (19, 21)) does not depend on this constant.

3 Results of test studies and discussion

We have applied the above formalism to characterize the evaporation processes in the vdW clusters aniline-(argon)$_n$ with n = 6–14 and (argon)$_n$ with n = 8–14 as a function of the initial parent internal energy. An adequate database to be used as a reference has been built by running MD simulations on the same cluster systems.

3.1 Procedures in MD simulations

Classical MD trajectories were generated by numerical integration of the Hamilton equations, using a fourth and fifth order Adams-Moulton predictor corrector respectively for the translational and rotational degrees of freedom. The typical time step for the integration scheme was equal to about 5 fs and the corresponding energy conservation was equal to around 0.001%. For the molecular cluster aniline-Ar$_n$ cluster, the aromatic chromophore has been kept rigid and its rotation in space has been described from the usual quaternion formalism [26]. The vdW potential was built as a sum of pairwise atom-atom Lennard-Jones potentials. For the aniline-Ar$_n$ clusters, the parametrisation for the atom-atom potentials can be found in previous papers [10,27]. For the pure Ar$_n$ clusters, we have used the Lennard-Jones parameters generally adopted, *i.e.* $\sigma = 3.405$ Å and $\epsilon = 83.26$ cm^{-1}.

The numerical scheme for the simulation of the dissociative trajectories has also been explained in previous papers [14,28]. Only a rapid description will be given here. At a given dissociation energy, a set of about 3 000 independent trajectories were used in order to obtain some confident statistical results. These trajectories were generated from initial conditions extracted from a MD simulation at lower energy (the corresponding kinetic temperature was equal to about 30 K). The parent cluster was considered as dissociated when one Ar atom was found at a distance from the center of mass of the whole system larger than 20 Å. The evaporation time was taken equal to the last time for which the radial velocity of the evaporated atom was negative, this procedure allowing to minimise the velocity effect on the calculation of the evaporation time. The evaporation rate was easily deduced from this set of trajectories by fitting the results to a first-order law (which governs the evaporation process in the classical approach). At the end of each dissociative trajectory, the release kinetic energy ϵ was obtained from the calculation of the two contributions.

First of all, the KER ϵ_{tr} is directly given by:

$$\epsilon_{\mathrm{tr}} = \frac{\mathbf{P}_{\mathrm{Ar}}^2}{2\mu} \tag{23}$$

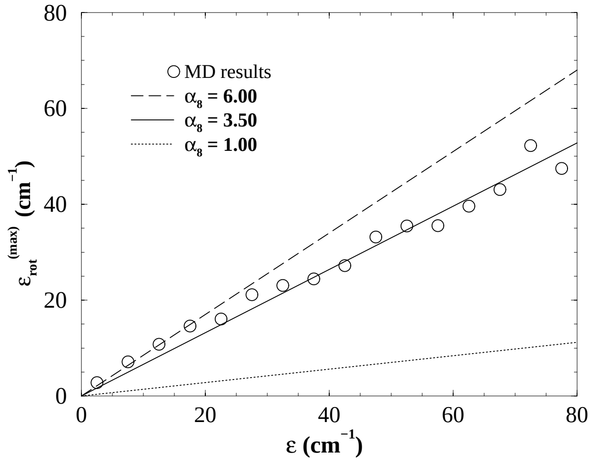


Fig. 1. The maximum value of the rotational energy release $\epsilon_{\text{rot}}^{(\text{max})}$ as a function of the total kinetic energy release ϵ. The open circles correspond to the MD results. Three straight lines are reported with different values for the α_8 parameter (see text).

in which $\mathbf{P}_{\text{Ar}}$ corresponds to the linear momentum of the evaporated Ar atom and μ is the reduced mass of the system (sub-cluster)–Ar.

The second contribution to the total kinetic energy release is the rotational energy of the sub-cluster. Due to the conservation of the total angular momentum in the dissociation process, and to the choice of a non-rotating parent cluster, the angular momentum of the sub-cluster ($\mathbf{J}_{\text{sc}}$) is given by:

$$\mathbf{J}_{\text{sc}} = -\frac{M_{\text{Ar}}}{\mu}\mathbf{J}_{\text{Ar}} \tag{24}$$

in which $\mathbf{J}_{\text{Ar}}$ is the angular momentum of the parent cluster and the evaporated Ar atom. Knowing $\mathbf{J}_{\text{sc}}$ and the inertia tensor $\tilde{I}_{\text{sc}}$ of the sub-cluster (calculated at the geometrical criterion), the rotational energy ϵ_{rot} can be easily obtained by:

$$\epsilon_{\text{rot}} = \frac{1}{2}\mathbf{J}_{\text{sc}} \cdot \left(\tilde{I}_{\text{sc}}^{-1}\mathbf{J}_{\text{sc}}\right). \tag{25}$$

Mean values were obtained by ensemble average over the set of trajectories.

3.2 Test of the assumptions

As explained in the previous section, the mean kinetic energy values (Eqs. (9, 19, 21)) but also the densities of probability (Eqs. (18, 20)) are obtained by making the assumption of the linearity of $\epsilon_{\text{rot}}^{(\text{max})}$ as a function of the total kinetic energy ϵ. This assumption has been tested by MD simulations. In Figure 1 is plotted $\epsilon_{\text{rot}}^{(\text{max})}$ as a function of ϵ in the case of the non-rotating aniline-Ar$_8$ parent cluster at a vibrational energy equal to 960 cm^{-1}. Open circles corresponds to the MD results and the three straight lines corresponds to the linear fit with different values of α_8.

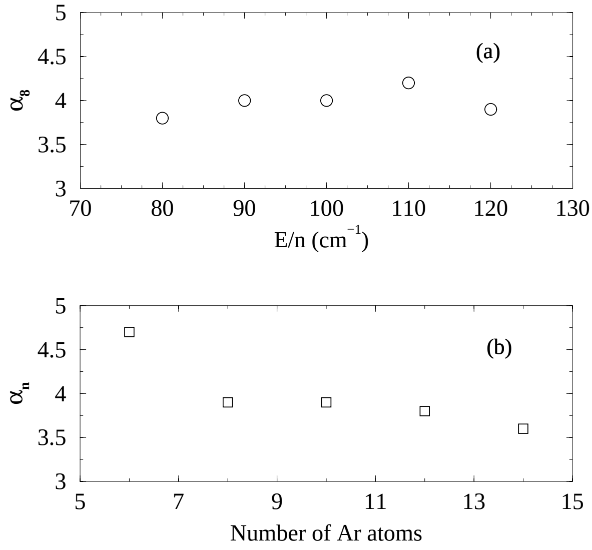
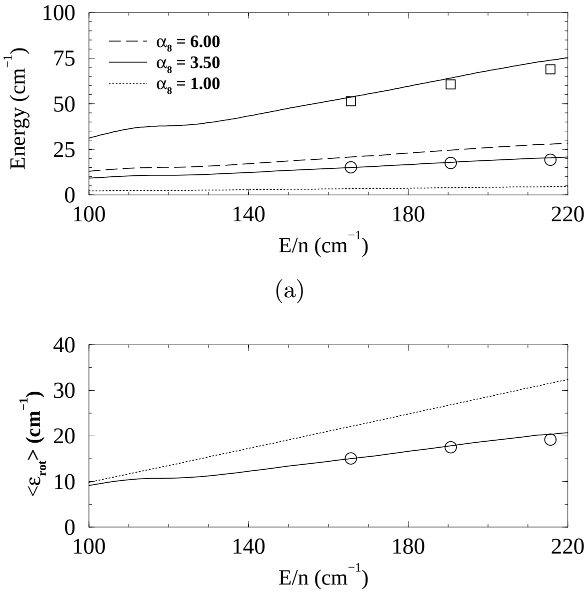


Fig. 2. (a) α_8 as a function of E/n in the case of the Ar$_8$ parent cluster; (b) α_n as a function of the number n of Ar atoms in the case of a pure vdW Ar$_n$ cluster at $E/n = 120$ cm^{-1}. All data are extracted from MD results.

First of all, the linearity of $\epsilon_{\text{rot}}^{(\text{max})} = f(\epsilon)$ is well verified in this vdW system. In the pure Ar$_n$ cluster (not shown here), the linearity is also a good approximation. The second point to note is that such MD simulations allow to obtain the value of α_n which is the *only parameter*, apart from vibrational densities of states, needed for the calculation of the rotational and translational distributions as a function of the parent total energy. However another assumption was to consider the slope of this curve as constant when the energy E, deposited in the parent cluster, was changed. In Figure 2a the value of α_8 has been reported for five different internal energies in the parent cluster Ar$_8$. On this plot it appears that this value is effectively almost constant and equal to 4.0 ± 0.2 (the uncertainty was deduced from that on the slope γ_n of the $\epsilon_{\text{rot}}^{(\text{max})} = f(\epsilon)$ curve).

The sensitivity of this parameter to the cluster size has also been explored (see Fig. 2b) from $n = 6$ to $n = 14$, and found small. Thus α_n appears as a very useful parameter whose value is rather robust. Physically it corresponds to the fact that when the evaporating atom is at a distance from the center of mass of the sub-cluster which is four times larger than the cluster radius, the fragments should be considered as fully separated. This maximum distance to locate the transition state seems quite reasonable in view of the smallness of the atom-sub cluster interaction in such a configuration.

As shown above it is easy to extract from MD simulations the value of α_n at high energy, *i.e.* the energy range for which the evaporation dynamics is fast enough to obtain confident statistical results. We are going to assume that this value is unchanged in the lower energy regime for which MD simulations cannot be used, but the evaporation dynamics can be characterized with the statistical model proposed in this paper.



(a)

(b)

Fig. 3. (a) Mean kinetic energy (open squares -MD- and upper curve) and mean rotational energy (open circles -MD- and lower curves) as a function of E/n in the case of the aniline-Ar$_8$ parent cluster; in (b) the harmonic model predictions for the mean rotational energy have been added in the dotted line.

3.3 Rotational and translational kinetic energy release

3.3.1 Aniline-Ar$_8$ cluster

The density of states of the aniline-Ar$_7$ cluster product has first been calculated from running Nosé trajectories (see end of Sect. 2). The mean total KER $\langle\epsilon\rangle$ has then been extracted from the calculation of the density of states of the product clusters and from equation (9). On the other hand the mean rotational energy $\langle\epsilon_{\rm rot}\rangle$ has been deduced from equation (19) using the vibrational density of states $\omega_{\rm v}^{(\rm p)}$ of the aniline-Ar$_7$ product cluster and the value $\alpha_8 = 3.50$ of the α_n parameter which is obtained from MD simulations as explained above (see Fig. 1). In Figures 3a and 3b the results (MD simulations and statistical model) are displayed in the case of the evaporation of the aniline-Ar$_8$ cluster. In Figure 3a are reported first the MD results for the mean total kinetic energy $\langle\epsilon\rangle$ (open squares) and for the mean rotational contribution (open circles). The dotted line corresponds to the calculation of $\langle\epsilon\rangle$ from equation (9). The three other curves correspond to the calculation of $\langle\epsilon_{\rm rot}\rangle$ with different values of the α_8 parameter: 1.00, 3.50 and 6.00. It is remarkable that a very good agreement is found when $\alpha_8 = 3.50$ which is in fact the value obtained from the fit of $\epsilon_{\rm rot}^{(\rm max)}$ as a function of ϵ (see Fig. 1). It indicates that the statistical model allows to reproduce the mean rotational energy quantitatively. In particular, it can be predictive in the low energy regime and thus bring quantitative informations in the energy range for which the evaporation time is in the microsecond domain. In Figure 3a, it can also be seen that the model predicts a non-linearity of $\langle\epsilon_{\rm rot}\rangle$ as a function of the internal energy. This effect, which appears around $E/n = 120$ cm^{-1}, is a direct consequence of the phase transition in the product aniline-Ar$_7$ cluster, as discussed in a previous paper [14].

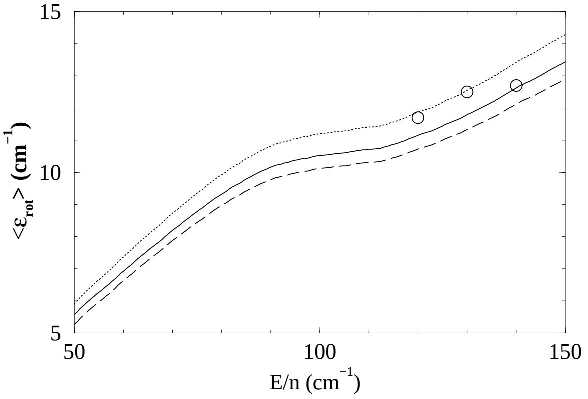


Fig. 4. Mean rotational energy for the Ar$_{14}$ parent cluster. The open circles correspond to the MD simulations. The three curves are obtained from the statistical model with $\alpha_{14} = 3.4$ (long dashed line), 3.6 (solid line) and 3.8 (dotted line).

We have also analysed the role of the anharmonicity in the quality of the agreement between MD results and the statistical model. Figure 3b shows the same results using an expanded scale, and we have added the predictions of the harmonic model (dotted line) by taking $\alpha_8 = 3.50$ in the both cases. As expected in the low energy regime, the anharmonic and harmonic models predict the same value. On the other hand at higher energy and in particular above the energy associated to the phase transition in the product cluster, a large discrepancy between the two models is found which demonstrates the necessity to take the anharmonicity into account in the statistical models describing the dissociation processes. Obviously the harmonic model gives a linear dependence of $\langle\epsilon_{\rm rot}\rangle$ as a function of the internal energy in the parent cluster.

3.3.2 Homogeneous argon clusters

The density of states of the Ar$_{13}$ cluster has been thoroughly studied. Thus we choose the parent cluster Ar$_{14}$ which evaporates into Ar$_{13}$ + Ar. In Figure 4 is shown the evolution of the mean rotational energy for the Ar$_{14}$ parent cluster. The value of α_{14} has been extracted from the fit of the $\epsilon_{\rm rot}^{(\rm max)}$ curve as a function of ϵ as explained above and given in Figure 2a. From this procedure, we have found $\alpha_{14} = 3.6 \pm 0.2$. Consequently, the statistical model has been applied with three values of α_{14} within these limits: $\alpha_{14} = 3.4$, 3.6 and 3.8. It clearly appears that the MD results are well reproduced by the model. In the same graph, it is also seen that the evolution of $\langle\epsilon_{\rm rot}\rangle$ as a function of the energy in the parent cluster is strongly altered around the phase transition in the Ar$_{13}$ product cluster (around $E/n = 100$ cm^{-1}). A similar behaviour has already been characterized for the evolution of the total kinetic energy release in the evaporation process [13,14].

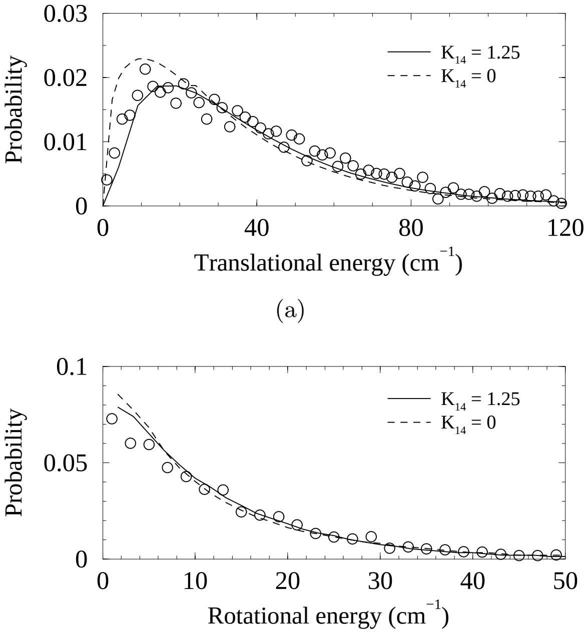
3.3.3 General remarks and distributions functions

The statistical model proposed in this paper allows to calculate the fraction of the KER devoted to the rotational excitation of the sub-cluster. If we analyse this fraction as a function of the energy for a given cluster size, we see that it slowly decreases as a function of the energy which is well reproduced by the statistical model. If now we look at the evolution of this fraction as a function of the cluster size for a given E/n, a clear decrease of this quantity is observed in the MD simulations when the number of Ar atoms increases. For the pure Ar_n clusters, we obtain $\langle\epsilon_{\mathrm{rot}}\rangle/\left(\langle\epsilon_{\mathrm{rot}}\rangle+\langle\epsilon_{\mathrm{tr}}\rangle\right)=0.33$, 0.29 and 0.25 respectively for $n=8$, 11 and 14 at $E/n=120\ \mathrm{cm}^{-1}$. Then for the small clusters, it is a large part of the energy release which is taken by the rotation of the sub-cluster. This point has to be carefully considered in particular in experiments which access the translational kinetic energy of the fragments. We suggest that the theoretical framework proposed in this paper can be usefully considered in kinetic energy experiments.

If we analyse now the mean translational energy derived from the model, it appears that this quantity is in fact underestimated when compared with MD results. We can relate this to the approximation $K_n=0$, since the translational kinetic energy tends to increase when K_n is increased (see Eq. (12)). If we include a non-zero value of K_n to get a better agreement between the mean values $\langle\epsilon_{\mathrm{tr}}\rangle$ and $\langle\epsilon_{\mathrm{rot}}\rangle$ from the model and from MD results, it is possible to derive a "best fit" value for the distance ratio β_n (see Eq. (13)). We found that β_n is always equal to about 3.0–3.5 in this range of cluster size ($n\approx 10$). In a pure atomic cluster, the cluster size R_{sc} of the product cluster can be approximated by $R_{\mathrm{sc}}=r_0(n-1)^{1/3}$ in which $2r_0$ is taken as the equilibrium distance between two atoms ($=2^{1/6}\sigma$ in a van der Waal cluster). The mean distance for the location of the transition state, R_{TS}, can be expressed as $R_{\mathrm{sc}}+Ar_0$. In the case of the Ar_{14} parent cluster, we found $\beta_{14}=3.35$ which corresponds to $A=5.7$. The value of β_{14} indicates that the transition state is located at a distance of about $5.5r_0$ from the surface of the spherical sub-cluster.

With this value of β_{14} we obtained the energy distributions plotted in Figure 5 making use of equations (19, 21). Also plotted are the MD results and the distributions derived within the $K_n=0$ approximation. The overall agreement is fairly good, but – as expected – the translational distribution is slighty better using $K_n\neq 0$. It is interesting to remark the rather low energy-peaked shape of this distribution.

As a final note it is of importance to stress that, apart from the vibrational densities of states, only one parameter has to be injected in the model. It is the parameter α_n derived from the slope γ_n of the curve $\epsilon_{\mathrm{rot}}^{(\mathrm{max})}(\epsilon)$ when $K_n=0$, it is replaced by the transition state distance ratio β_n when $K_n\neq 0$.



(a)

(b)

Fig. 5. (a) Distribution of the sub-cluster rotational energy; (b) distribution of the translational energy release in the case of the Ar_{14} parent cluster at $E/n=140\ \mathrm{cm}^{-1}$. The dashed lines correspond to the $K_n=0$ approximation (see text); the open circles to the MD results.

4 Conclusion

A novel extension of the phase space theory has been proposed here in order to evaluate the energy partition between the rotation of the remaining sub-cluster and the translational kinetic energy release in the evaporation process. This model has been successfully applied to the aniline-Ar_n and to the Ar_n clusters. It allows to reproduce quantitatively the numerical results obtained from molecular dynamics simulations. The ability of the model to predict the low energy regime allows to calculate the mean rotational energy of the sub-cluster in the energy range for which the dynamics of dissociation is too slow for estimations with MD simulations. A net "accident" in the evolution of the mean rotational energy is seen around the phase transition in the product cluster. Distributions of the rotational and translational energies can be directly extracted for any initial total energy in the parent from the knowledge of the density of states of the product cluster and by using a simple relation which gives the parameter β_n as a function of the cluster size. This last parameter, which governs the boundaries in the integration over specific energies, involves the ratio between the critical "separation" distance (or transition state) R_{TS} and the cluster radius R_{sc}.

In the case of pure atomic clusters, a general empirical law can be found for the evolution of the β_n parameter as a function of the cluster size. Indeed R_{sc} and R_{TS} can be evaluated by $R_{\mathrm{sc}}=r_0(n-1)^{1/3}$ and by $R_{\mathrm{TS}}=R_{\mathrm{sc}}+5.5r_0$. Consequently, the β_n parameter is deduced from the relation $\beta_n = 1 + 5.5(n-1)^{-1/3}$. Thus the model can be easily used to calculate the translational and rotational distributions of kinetic energy release resulting from the evaporation of pure atomic clusters as soon as the vibrational density of states of the product cluster can be evaluated. The validity of this relationship is expected to be better for large clusters for which the cluster size R_{sc} is relatively well reproduced by $R_{\mathrm{sc}} = r_0(n-1)^{1/3}$.

The foreseen interest of this model is to bring the last missing link between theory of evaporation and experiments: it is expected that experiments measuring the translational kinetic energy release can be tested soon against the predictions of this model.

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