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Collisional energy transfer modeling in non-equilibrium condensing flows

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Abstract. Molecular dynamics and DSMC models for energy transfer in argon dimer - argon monomer collisions are compared. The inelastic collision number for these collisions is evaluated, and found to decrease significantly when gas temperature increases.

Keywords: Homogeneous condensation, energy transfer, molecular dynamics, DSMC

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INTRODUCTION

Theoretical, experimental, and computational studies of homogeneous condensation has drawn much attention over the last decades, mainly because this phenomenon plays an important role in many atmospheric and technological processes, and understanding of its physical mechanisms and dependencies is critical for a number of engineering applications. One of such applications, pertaining to post boost vehicle operations at very high altitudes, is related to thruster plume expansion into surrounding rarefied atmosphere [1]. Condensation in the rapidly expanding flows has been observed experimentally as early as mid-30s [2], and has been extensively studied in the following decades (see for example [3] and the references therein). Computational modeling of expanding condensing flows has a shorter, although still a respectable history. In the past, two different approaches have been used to describe homogeneous condensation and, in particular, cluster nucleation (formation of small clusters from monomers) in non-equilibrium environment of rapid expansions. The first approach is based on the classical nucleation theory, and is in fact a macroscopic approach that uses equilibrium thermodynamics and the principle of detailed balance to calculate the cluster size evolution and properties.

The second approach is a kinetic, microscopic approach, often based on the direct simulation Monte Carlo (DSMC method) to describe the flow behavior. The DSMC method has been used to study the process of cluster formation and evolution for a number of years. Over the last decade, it has been extensively and successfully applied to modeling the processes of cluster formation and evolution in supersonic jets by Levin et al. (see, for example, [4, 5]). The model initially was based on the classical nucleation theory, with the new clusters being formed at the critical size. Further work of these authors [4] extended the kinetic dimer formation approach of Ref. [6], where it was assumed that a ternary collision always results in a dimer formation, to include molecular dynamic (MD) simulations for obtaining information on the probability of dimer formation in such ternary collisions.

More recently, the first principle kinetic theory was used [7] to construct a DSMC based model that uses a truly kinetic RRK algorithm [8] to characterize the cluster evaporation rates, and an energy dependent collision procedure similar to the recombination reaction model of Ref. [9] for the collision complex formation. An empirical parameter was introduced for the inelastic collision number in the cluster-monomer collisions, and the Larsen-Borgnakke (LB) principle was extended to simulate the energy transfer in collisions among monomers and clusters. This principle was also used for the energy redistribution in the dimer formation process. The model [7] was then adapted and extended to a combined Lagrangian-Eulerian approach [10], that maintain the benefits of a kinetic treatment of the homogeneous nucleation process while having a significantly higher computational efficiency than a DSMC based method.

The recent studies have shown that while the application of the kinetic approach has a number of benefits, which include but limited to capturing non-equilibrium features of the condensation process and correct prediction of many condensation phenomena and rates (see, for example, Refs. [7, 11]), they do suffer from large uncertainties in such key

parameters that they use as heat capacities, binding energies, energy redistribution mechanism, and cluster inelastic collision number. Some physical parameter uncertainties have been clarified in the previous paper [11], although the energy redistribution mechanisms in cluster formation and monomer-cluster collisions are still largely unknown.

The main objective of this work is the study of the energy transfer between translational and internal modes in collisions between small argon clusters and monomers, evaluation of the applicability of the Larsen-Borgnakke model to simulate this transfer, and analysis of the impact of this transfer on expanding plume flows. The molecular dynamics method is used to compute energy redistribution after argon cluster - monomer collisions, and the Lagrangian-Eulerian approach [10] is employed for the plume flow analysis.

IMPACT OF THE INTERNAL ENERGY TRANSFER RATE

It has been previously noted [7] that the transfer of energy between translational and internal modes in collisions between dimers and monomers has a strong impact on the dimer equilibrium constant. The reason for this effect is that the dimer-monomer collisions are the principal factor that changes dimer internal energy. Dimer internal energy distribution, in turn, directly affects the dimer dissociation rate and, therefore, the equilibrium constant. The dimer dissociation is an endothermic process, and may be considered as a result of unimolecular dissociation of Ar_2 clusters that have internal energy larger than the binding energy of the clusters. It is obvious that the lower the dimer binding energy, the larger the impact of the dimer internal energy relaxation rate. It was found in Ref. [7], where the cluster internal energy relaxation number Z was introduced, similar to the rotational and vibrational relaxation numbers of gas molecules, that Z has a much stronger influence on the argon cluster nucleation process than on water cluster nucleation. This was related to the Ar_2 binding energy E_b of 1.98×10^{-21} J, as compared to water dimer E_b of 1.98×10^{-21} J. Even though water dimers have a significantly larger heat capacity than argon dimers, it still takes on average much more collisions to increase the internal energy E_{int} of a stable water dimer that is initially formed with $E_{int} < E_b$.

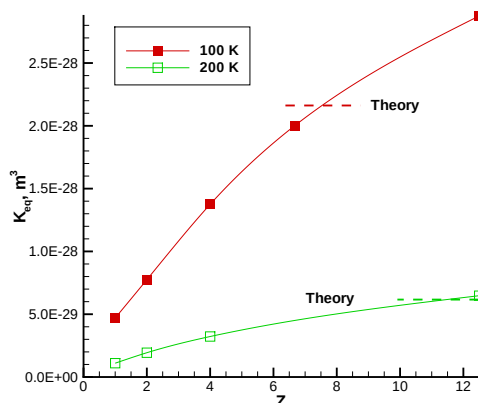


FIGURE 1. Impact of cluster internal energy relaxation rate on equilibrium constant and comparison with theoretical predictions [12].

For stable argon dimers, it typically takes only few collisions to exceed E_b . Although dimers with after-collision internal energy larger than the binding energy do not dissociate immediately after collision, their lifetime (the RRK model [13] may be used to estimate the cluster lifetime) is typically shorter than the mean collision time. This makes the dissociation of dimers with $E_{int} > E_b$ likely. The impact of Z on the argon dimer equilibrium constant K_{eq} is illustrated in Fig. 1, where the model [7] is used to calculate K_{eq} in a thermal bath of pure argon with a density of 1.326 kg/m^3 . Note that the dependence on gas density in this case is negligible, since the mean collision time is much larger than the average cluster lifetime. The value of Z was varied from 1 to 12.5 for two gas temperatures. As expected, the increase of Z results in significant increase of the equilibrium constant. The dependence on Z is almost linear at small Z , but becomes weaker as Z increases. This is because the monomer-dimer sticking becomes dominant for $Z \gg 1$ (the sticking coefficient was 0.06 for this case). As seen from the figure, the selection of an optimum value

TABLE 1. Inelastic collision number for different gas temperatures.

T, K	0.0	100.0	200.0	300.0	400.0	500.0
Z^{-1}	0.25	0.13	0.08	0.06	0.046	0.04

of Z that provides best agreement with the theoretical results of Ref. [12] depends on thermal bath temperature. It is about 7 for 100 K and 12 for 200 K. The temperature dependence used in Ref. [11] is summarized in Table 1.

NUMERICAL APPROACH

A general chemical dynamics program VENUS [14] has been used in molecular dynamics simulations. The Morse pairwise potential was applied to described the inter- and intra-cluster interactions of argon atoms. Note that although this is a less accurate interaction potential than a more sophisticated HFDID1 potential [15], it has very similar bonding energy, and is expected to provide qualitatively similar results. The Morse potential is represented in its standard form

$$V(r) = D(\exp(-2\alpha(r - r_e)) - 2\exp(-\alpha(r - r_e)))$$

with the following parameters taken from [16]: $\alpha=0.908597$, $D=99 \text{ cm}^{-1}$, $r_e=3.757 \text{ \AA}$. Trajectories started at a separation of $13\text{\AA}$ between dimer center of mass and impinging atoms. The convergence of cross section for various impact parameters and number of trajectories was studied, and for typical runs maximum impact parameter of $10\text{\AA}$ was used, and 20000 trajectories were run. Trajectories were terminated when the distance between the dimer center of mass and impinging atom was $13\text{\AA}$.

The gas flow was simulated with the DSMC code SMILE [17] where the first-principle model [7, 11] was incorporated. Some changes were introduced in the parameters of the approach that are believed to more accurately reproduce the physics of the dimer formation phenomenon. Namely, Lennard-Jones parameters used in the expression [18] to estimate the collision complex lifetime are $\epsilon = 1.98 \times 10^{-21} \text{ J}$ and $\sigma = 3.405 \text{ \AA}$. The monomer vibration frequency in argon clusters was found to be $2.6 \times 10^{11} \text{ s}^{-1}$. Finally, the dimer stabilization probability of 0.2 was used.

AFTER-COLLISION ENERGY REDISTRIBUTION

Previous model [7] assumed the Larsen-Borgnakke type energy redistribution after inelastic argon monomer-dimer collisions, with the inelastic collision number Z fitted to match the dimer formation equilibrium constant as a function of temperature (see Table 1). While this approach appears reasonable for preserving correct dimer mole fractions at equilibrium, it does not guarantee proper energy distributions, trimer and larger cluster formation rates, or even dimer formation rates in non-equilibrium plume flows. In order to analyze the reliability and applicability of this approach, more accurate analysis is necessary, such as that of trajectory calculations with a realistic interaction potential.

The profiles of after-collision internal (the sum of rotational and vibrational) energy of argon dimers is presented in Fig. 2 for two different approaches, the molecular dynamics trajectory calculations and the Larsen-Borgnakke collision algorithm. The calculations were conducted for the initial vibrational level $v = 2$ and rotational level $J = 20$ and the Maxwellian distribution of relative collision velocities at a temperature of $T^* = 2$. Here T^* is the temperature normalized by the reduced argon dimer bond energy of $E_b/k = 143.2 \text{ K}$. Only dimer-monomer collisions that resulted in net dimer internal energy change were considered for this plot. It is seen that there is a qualitative difference in the after-collision distributions, as the MD collision tend to cause only a small change in the dimer internal energy, whereas the LB approach results in a Boltzmann distribution at a local temperature of about 185 K.

Note that stable dimers are those with the internal energy smaller than E_b , that is the particles that fall to the left of $E_b/k = 143.2 \text{ K}$ in the after-collision energy distribution profile. The dimers with internal energy in excess of E_b are unstable and may dissociate before the next binary collision. Note that the time to dissociation may be estimated, for example, using the RRK model or more sophisticated, and is generally on the order of the inverse dimer vibration frequency of $2.6 \times 10^{11} \text{ s}^{-1}$. For a 1 atm and 300 K argon gas, where the dimer mean collision time is on the order of 10^{-10} s , most of unstable dimers will dissociate before the next collision. In order to create the same number of unstable dimers after a single collision, a parameter Z needs to be used in the LB procedure, so only a fraction $1/Z$ leads to the internal energy transfer. The use of Z will result in a proportional decrease of the dashed line in Fig. 2, but will not change the equilibrium shape of that curve, characterized by relatively large population of high-energy tail.

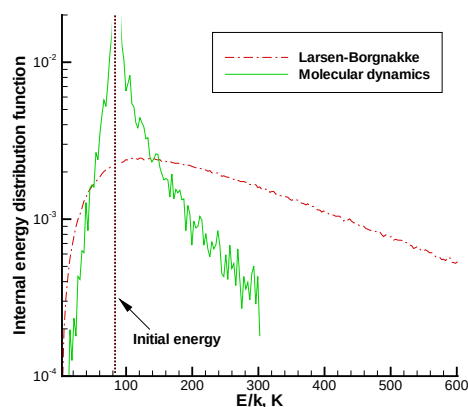


FIGURE 2. After-collision internal energy redistribution in inelastic LB and MD collisions. Initial internal energy levels are $v=2$, $J=20$ ($E/k = 83.4$ K).

DIMER BREAKUP CROSS SECTIONS IN DIMER-MONOMER COLLISIONS

The argon dimers are characterized by fairly low binding energy, which results in high probability of formation of unstable dimers after dimer-monomer collisions, followed by dimer breakup. Therefore, it is important to analyze the stable-to-unstable (or dimer breakup) collision cross sections at different gas temperatures. From these collision cross sections, obtained with the MD approach, the inelastic collision number for dimer-monomer collisions may be evaluated for a given intermolecular potential that specifies the total collision cross section (such as the VHS model in DSMC). Consider first the impact of the vibrational level v and the rotational level J of a colliding argon dimer on the cross section of a process that transforms a stable dimer with the internal energy $E_{int} < E_b$ to an unstable dimer with $E_{int} < E_b$. The MD results obtained for different v and J are shown in Fig. 3. The obtained cross sections are close to the total collision cross section of $80\text{\AA}^2$ calculated using the VHS model. As expected, the cross section generally increases with rotational and vibrational level, which reflects the increase of the dimer breakup probability with the available internal energy of the colliding dimer. Note that the stable-to-unstable dimer cross section is more sensitive to the change in vibrational level, Fig. 3 (left), where the energy quantum is larger; the cross section increase is relatively insignificant for small rotational numbers, Fig. 3 (right), since the J^2 dependence of the internal energy.

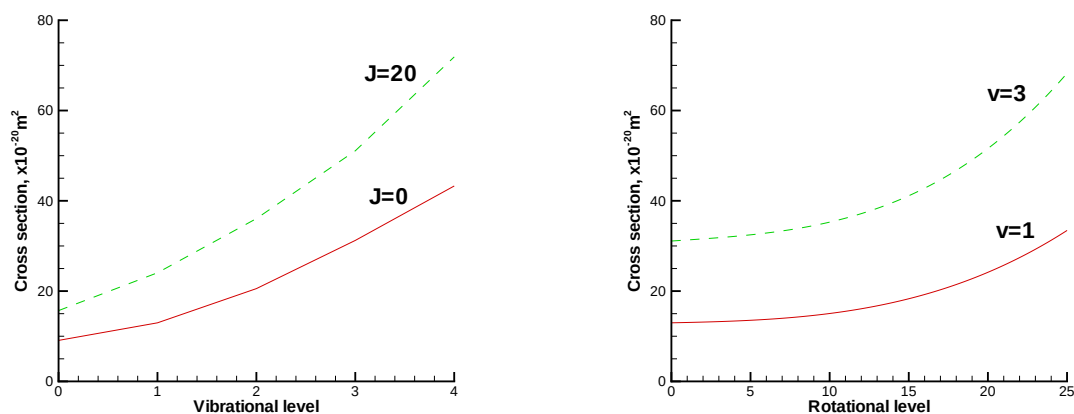


FIGURE 3. Stable-to-unstable dimer cross section as a function of changing vibrational (left) or rotational (right) level. $T^* = 0.5$.

The increase of the cross section with the rotational quantum number is more pronounced at lower temperatures, as illustrated in Fig. 4 (left). This is related to the fact that at $T^* = 2$, the average relative translational energy is noticeably

larger than E_b , and thus the pre-collision rotational energy is relatively less important than for $T^* = 0.5$. The average internal energy of stable dimers changes between $E_{int}/k = 78$ K and $E_{int}/k = 92$ K, and the dimer breakup cross section for a typical internal energy of 84 K ($v = 2$ and $J = 20$) is shown in Fig. 4 (right). It is interesting to note that the breakup cross section practically does not change after $T^* \approx 1$. This indicates that dimer breakup probability, which is the ratio of the breakup cross section to the total collision cross section σ_{tot} , will only be a function of σ_{tot} at $T \approx 140$ K. For a lower internal energy ($v = 2$ and $J = 4$), the temperature dependence is more noticeable, but still relatively weak.

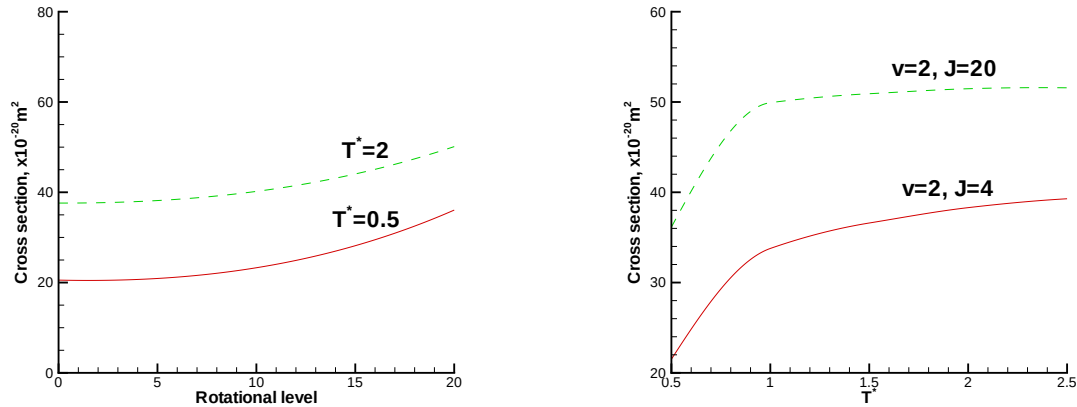


FIGURE 4. Stable-to-unstable dimer cross section for $v = 2$ and two different translational temperatures (left) and for two different internal states and varying translational temperature (right).

DIMER BREAKUP AND INELASTIC PROBABILITIES

The most important outcome of collisions between stable droplets and monomers is the formation of unstable dimers with internal energy larger than the binding energy, since such a formation is the main mechanism of droplet breakup. Its impact on dimer population will in turn influence the population of larger clusters, that are created through sticking and coalescence of dimers. For the condensing gas modeling to be reliable, it is important to implement correct rates of droplet breakup. If one assumes that for maintaining correct rates of droplet breakup it is sufficient to have realistic number of stable-to-unstable dimer collisions for any given internal energy, then the key issue is to maintain correct droplet breakup cross sections.

For a kinetic condensation model that is based on the VHS total collision cross sections and the LB energy redistribution algorithm, that means that the value of the inelastic collision number Z should be chosen from the relation $Z^{-1} = \phi = \sigma_{ref}/\sigma_{LB}$, where ϕ is the probability of the collisional energy transfer that results in the formation of an unstable dimer, σ_{ref} is the reference dimer breakup cross section that may be obtained, for example, from molecular dynamics simulations, and σ_{LB} is the dimer breakup cross section in a single VHS collision that has an LB energy transfer between all translational and internal energy modes. The results of calculation of ϕ for different rotational and vibrational levels and translational temperatures are summarized in Table 2.

Two conclusions may be drawn from that table. First, the MD calculations indicate that for a given internal energy, the dimer with a higher vibrational energy will break up with higher probability (vibrational favoring). Second, and most importantly, for given vibrational and rotational levels, the inelastic collision number Z defined as $Z = \sigma_{LB}/\sigma_{MD}$ significantly increases when temperature increases. For example, for the reduced internal energy of 83.89 K, $\phi = 1/Z$ decreases by almost a factor of 4, from 1.18 to 0.3, when the gas temperature increases from $T^* = 0.5$ to 2. Similar temperature dependence is observed when Z is calculated in a conventional manner based on energy relaxation to equilibrium value. Note that for larger dimer internal energies, the values of ϕ become larger than unity, which is related to incorrect after-collision energy redistribution in the LB approach, as was discussed in the previous section.

While the values of ϕ calculated as $\phi = \sigma_{MD}/\sigma_{LB}$ may be directly used in modeling condensing flows with a kinetic approach such as that of Ref. [7], the use of the LB technique for energy transfer in dimer-monomer collisions results in drastically different from MD energy redistribution, which may lead to inaccurate results. Therefore, it is better

TABLE 2. Droplet breakup cross sections for different internal energies

v	J	$E_{int,k}, \text{K}$	$\sigma_{MD}, \text{\AA}^2$	$\sigma_{VHS}, \text{\AA}^2$	$\sigma_{LB}, \text{\AA}^2$	ϕ
$T^* = 0.5$						
0	0	11.71	9.08	112.64	15.22	0.60
0	10	20.87	10.71	112.64	16.70	0.64
0	20	46.11	15.68	112.64	21.45	0.73
0	30	85.60	32.83	112.64	30.92	1.06
2	0	53.53	20.55	112.64	23.03	0.89
2	10	61.64	23.31	112.64	24.87	0.94
2	20	83.89	36.06	112.64	30.45	1.18
2	30	115.82	70.07	112.64	39.79	1.76
4	0	87.32	43.29	112.64	31.39	1.38
4	10	94.32	48.69	112.64	33.37	1.46
4	20	113.25	71.88	112.64	38.99	1.84
$T^* = 2$						
2	0	53.53	37.64	226.26	160.88	0.23
2	10	61.64	40.36	226.26	162.80	0.25
2	20	83.89	50.13	226.26	167.99	0.30
2	30	115.82	81.78	226.26	175.06	0.47

to evaluate ϕ from comparison with equilibrium dimer formation rates, and select the values that provide a good agreement with available theoretical results. It was found from comparison with theoretical analysis [12] that $\phi = 0.2$ for equilibrium gas at $T^* = 0.7$, 0.11 for $T^* = 1.4$, and 0.08 for $T^* = 2.1$. This presents a temperature dependence similar to that obtained with $\phi = \sigma_{MD}/\sigma_{LB}$, although smaller magnitude of the inelastic collision probability.

CONCLUSIONS

The molecular dynamics calculations of energy transfer in argon dimer-monomer collisions, with emphasis on collisions that result in formation of unstable dimers with internal energy larger than the binding energy. Comparison with the energy transfer algorithm based on VHS and Larsen-Borgnakke models for total and inelastic cross sections indicate that the inelastic collision number decreases strongly with temperature. The large difference between the after-collision internal energy distributions in MD and LB models, as well as the presence of vibrational favoring in MD, indicate to potential problems when using the LB model for energy transfer in droplet-monomer collisions.

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