Nonequilibrium internal energy distributions during dissociation

Narendra Singh and Thomas Schwartzentruber

*Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN 55455

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In this work, we propose a model for nonequilibrium vibrational and rotational energy distributions in nitrogen using surprisal analysis. The model is constructed by using data from direct molecular simulations (DMSs) of rapidly heated nitrogen gas using an ab initio potential energy surface (PES). The surprisal-based model is able to capture the overpopulation of high internal energy levels during the excitation phase and also the depletion of high internal energy levels during the quasi-steady-state (QSS) dissociation phase. Due to strong coupling between internal energy and dissociation chemistry, such non-Boltzmann effects can influence the overall dissociation rate in the gas. Conditions representative of the flow behind strong shockwaves, relevant to hypersonic flight, are analyzed. The surprisal-based model captures important molecular-level nonequilibrium physics, yet the simple functional form leads to a continuum-level expression that now accounts for the underlying energy distributions and their coupling to dissociation.

nonequilibrium distribution | surprisal analysis | high-temperature thermochemistry | shock waves | hypersonic flows

High-temperature, chemically reacting gas systems are inherently nonequilibrium. As an example, dissociation reactions are coupled to the vibrational energy of the dissociating molecule. Molecules in high vibrational energy states (high \( v \) levels) are strongly favored for dissociation, leading to a population depletion compared with the corresponding equilibrium (Boltzmann) distribution. This depletion is balanced by nonreactive collisions within the gas that act to repopulate these high \( v \) levels via translational–vibrational excitation. Rotational energy states (\( j \) levels) are similarly coupled to dissociation, although to a lesser extent than vibration. As a gas is undergoing dissociation, this combination of depletion due to dissociation and excitation due to translational–internal energy transfer leads to a quasi-steady-state (QSS) where the internal energy distribution functions (both rotation and vibration) are time-invariant and non-Boltzmann. Furthermore, when a gas is rapidly heated, such as behind a strong shockwave, high \( v \) levels can become overpopulated compared with the corresponding Boltzmann distribution as energetic collisions lead to multiquantum jumps in vibrational energy. Since high \( v \) and \( j \) levels are strongly favored for dissociation, the precise nonequilibrium distributions of internal energy can significantly affect the gas dissociation rate.

Continuum models used to analyze reacting gas flows, such as the Navier–Stokes equations extended for thermochemical nonequilibrium (1, 2), model only average molecular energies. In some cases, it is appropriate to use a temperature \( T \) assuming equipartition of energy across available translational, rotational, and vibrational energy modes. In other cases, such as for hypersonic flows, thermal nonequilibrium is modeled by using a combined translational–rotational temperature \( (T_{tr}) \) and a separate vibrational temperature \( (T_v) \) (3–8). However, since these parameters represent averages of the molecular energy distributions, they do not explicitly account for non-Boltzmann distributions and their coupling to dissociation. Rather, when such multitemperature models are parametrized by using experimental data, non-Boltzmann effects are captured empirically. As a result, the parametrized model may not be accurate when extended to other nonequilibrium conditions beyond the limited experimental data it was fit to.

In this work, we develop a continuum-level model that now explicitly captures non-Boltzmann internal energy effects and coupling to dissociation. This work is made possible by recent advances in ab initio potential energy surfaces (PESs) for high-temperature air, by a direct molecular simulation (DMS) capability enabled by high-performance computing, and ultimately by a surprisal-analysis model formulation parametrized by using the new ab initio data. We focus on modeling thermochemical nonequilibrium processes behind strong shockwaves with application to hypersonic flows; however, the modeling approach may be more widely applicable to other gas systems in nonequilibrium.

**Ab Initio Results**

Recently, for the purpose of studying air chemistry under hypersonic flow conditions, accurate PESs for \( \text{N}_2–\text{N}_2 \) and \( \text{N}–\text{N}_2 \) collisions (9), \( \text{O}_2–\text{O}_2 \) (10) and \( \text{O}–\text{O}_2 \) (11) collisions, \( \text{N}_2–\text{O}_2 \) collisions (12), and \( \text{N}_2–\text{O} \) collisions (13) have been developed by using methods from quantum mechanics. Given the spatial configuration of all atoms at any instant during a collision, the multidimensional PES is used to evaluate the force acting on each atom. In this manner, a collision between molecules can be time-integrated starting from an initial condition by using the classical equations of motion. The standard procedure is referred to as quasi-classical-trajectory (QCT) analysis (14, 15), since, although the initial internal energy states may correspond to quantum states, the time integration is performed by using classical mechanics, and therefore postcollision internal energies are not quantized.

Typically, QCT analysis is performed for large numbers of collisions with initial conditions corresponding to properly randomized atomic orientations (impact parameters) and corresponding to desired precollision translational energy and internal energy states. Such QCT analysis is generally used to determine

**Significance**

Predicting the extent of air dissociation in thin shock layers created by hypersonic vehicles is challenging due to coupling between gas internal energy and chemical reactions. Thermochemical nonequilibrium flow models, capable of predicting the heat flux and the flux of reactive atomic species to the vehicle surface, are critical for heat shield design. Whereas existing continuum models do not account for non-Boltzmann rotational and vibrational energy distributions and coupling to dissociation, we develop a model based on recent ab initio calculations that does.

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To whom correspondence should be addressed. Email: singh455@umn.edu.
rovibrational state-specific transition rates (16–21). If a distribution of precollision states is imposed—for example, Maxwell–Boltzmann distributions—then thermally averaged excitation and dissociation rates can be computed as a function of temperature for instance as done by Bender et al. (22) (N(4S) + NO(4Π) + NO(4Π)), and Varandas and coworkers (24–26) [N(2D) + N2, N(2Σ) + NO(X2Π)]. Apart from QCT, purely quantum dynamics approaches (27–29) can also be used to obtain thermal rate constants, as done by Meuwly and coworkers (29) to study the NO(2Π) + NO(4Π) interaction for conditions relevant to hypersonic flows. However, to compute the evolution of a reacting gas, including non-Boltzmann internal energy distributions, the set of state-specific transition rates must be incorporated into master equation analysis. Unfortunately, full master equation analysis is computationally expensive, even for atom–diatom systems (≈10⁷ rovibrational transitions for N–N₂ collisions (30)) and is intractable for diatom–diatom systems (≈10¹⁵ transitions for N₂–N₂ collisions).

Recently, this problem has been overcome by the capability to perform DMS of an evolving gas system, where the only model input is the PES (or set of PESs), and precomputed state transition rates are not required. Essentially, the DMS method embeds trajectory calculations within a molecular simulation of the gas [specifically the direct simulation Monte Carlo (DSMC) particle method (31, 32)]. DMS maintains the accurate stochastic treatment for dilute gases exploited by DSMC; however, it replaces stochastic DSMC collision models with trajectory calculations performed on a PES. In this manner, a molecule’s post-collision state becomes its precollision state for a subsequent trajectory calculation. The result is a direct simulation of rovibrational excitation and dissociation including all relevant physics. DMS is equal in accuracy to full master equation analysis using rates from QCT calculations (33); however, DMS is tractable for the full nitrogen system (both N–N₂ and N₂–N₂ collisions). The DMS method was originally proposed by Koura (34–36), and it is noted that similar approach have been used by Bruehl and Schatz (a sequential QCT approach) (37, 38) and Hase and coworkers (39) (a pure molecular dynamics approach). The method was implemented by using modern DSMC algorithms by Norman et al. (40) and extended to rotating, vibrating, and dissociating molecules by using ab initio PESs in a series of articles by Valentini et al. (15, 33, 41, 42). The details of the DMS method have been summarized in a recent review article by Schwartzentruber et al. (43).

Fig. 1 shows an example DMS result where a zero-dimensional system containing 1 million N₂ molecules is initialized corresponding to average rotational and vibrational energies of \( \langle \epsilon_{rot} / k_B \rangle = \langle \epsilon_v / k_B \rangle = 2000K \); however, the center-of-mass translational energies of the molecules is maintained at \( T = 20,000 \text{ K} \) (by resampling/resetting at each timestep). This is representative of the conditions immediately behind a strong shockwave where the relative translational energy is very high and the internal energy of the gas requires a finite time to excite, ultimately leading to dissociation.

In Fig. 1, the average internal energies \( \langle \epsilon_{rot} \rangle, \langle \epsilon_v \rangle \) are seen to increase and reach a QSS during which the gas continues to dissociate. Fig. 2 shows the evolution of the vibrational energy distribution function for this simulation. As discussed previously, initially high \( ν \) levels are overpopulated, and later during QSS they are depleted, compared with the corresponding Boltzmann distribution based on the average vibrational energy. Such depletion has been shown to reduce the computed dissociation rate in nitrogen by approximately three to five times compared with that computed by QCT using a Boltzmann distribution (22, 33). This is due to strong coupling between vibrational energy and dissociation, shown by the circular symbols in Fig. 2. Specifically, by analyzing the molecules that dissociate during a DMS calculation, it is evident that, per collision, the probability of dissociating from a high \( ν \) level is three orders of magnitude higher than dissociating from a low \( ν \) level. Therefore, even small variations in the vibrational energy distribution can lead to noticeable differences in the overall dissociation rate. Nitrogen dissociation rates computed in QSS by the DMS method have been shown to agree well with existing experimental data taken in shock-tube facilities (15, 42). Recent DMS results for oxygen systems (10) exhibit similar trends (44) and also agree well with experimental data.

Below, we use recent DMS results to construct and validate a continuum-level model that captures the evolution of non-Boltzmann internal energy distributions and coupling to dissociation.

Before proceeding, it is important to note that DMS operates only on the position and velocities of atoms (whether bonded within a molecule or not) and therefore makes no assumption about decoupling rotational and vibrational energy. Such decoupling is only performed as a postprocessing step to guide reduced-order modeling. In this work, we follow the vibrational prioritized approach of R. L. Jaffe (45), explained in detail for our trajectory calculations in ref. 22. This vibrational prioritized approach is used, along with the PES, to determine \( \langle \epsilon_{rot}, \epsilon_v \rangle \) and \( \langle \epsilon_{r,i}, \epsilon_{v,i} \rangle \) from the positions and momenta of DMS atoms bound within molecules.

**Model Framework: Surprisal Analysis**

We choose to model nonequilibrium internal energy distributions using surprisal analysis (46, 47). The surprisal, \( I(i) \), is a measure of deviance of an observed distribution \( f \) from a prior distribution \( f_0 \). In our case, \( f \) is the nonequilibrium internal energy distribution during excitation and QSS (seen in Fig. 2), whereas \( f_0 \) is the equilibrium distribution corresponding to the maximum entropy state. Mathematically,

\[
I(i) = -\log \left( \frac{f(i)}{f_0(i)} \right) .
\]  

Essentially, \( I(i) \) is a measure of entropy deficiency, which is minimized subject to constraints acting on the system. The surprisal can be expressed in terms of constraints in the following manner:

\[
I(i) = \lambda_0 + \sum_{r=1}^{m} \lambda_r A_r(i),
\]

where \( A_r(i) \) are the set of \( m \) properties for the state \( i \).

Surprisal analysis (also known as information theoretic analysis) (46–48) has been used in many fields, including recently presented in a recent review article by Schwartzentruber et al. (43).
The surprisal is seen to be negative when the average internal energy (⟨εi⟩ in Fig. 3 and ⟨εrot⟩ in Fig. 4) is low, indicating overpopulation compared with the equilibrium distribution. This corresponds to the early phases of excitation in Fig. 1. The surprisal becomes positive when the average internal energies are high, corresponding to the QSS region in Fig. 2 when the gas is rapidly dissociating. What is most interesting is that the surprisal is approximately linear over a wide range of internal energy levels (0.15 < εi/εd < 0.8). It is important to note from Fig. 2 that the population of molecules with εi/εd > 0.8 becomes vanishingly small, and therefore this portion of the distribution function has a limited effect on the overall system. The nonlinear nature at very high energies is a consequence of (i) when the average vibrational energy is low, the population of molecules in high-energy states becomes vanishingly small; and (ii) such high-energy vibrational states have strong rotation to rotational energy.

To be concise, we have only shown the case of excitation to 20,000 K. However, DMS results have been analyzed for a range of temperatures between 10,000 and 30,000 K for nitrogen systems involving only N2–N2 collisions and systems involving both N2–N2 and N–N2 collisions (52). In all cases, the surprisal trends are similar. The linear nature of the surprisal functions suggests that a simple model can be constructed to accurately represent the nonequilibrium internal energy distributions.

**Model Formulation**

Ideally, a model for the nonequilibrium distributions should be constructed by using average energy parameters only so that the model can be incorporated into continuum-level analysis. These parameters include the average internal energy per molecule, ⟨εi⟩, and ⟨εrot⟩, and the average translational energy per molecule, (3/2)kBT = ⟨εt⟩, where T is the translational temperature of the gas.

**QSS Distributions.** For vibration, we propose the following model form for the surprisal in the QSS regime:

$$-\log \left( \frac{f(v)}{f_0(v)} \right) = \lambda_0 + \lambda_1 \frac{v}{\epsilon_d} v,$$

where λ0, v, and λ1,v are constants. The main feature of this simple model is the linear dependence on v level and that the states. The surprisal is seen to be negative when the average internal energy (⟨εi⟩ in Fig. 3 and ⟨εrot⟩ in Fig. 4) is low, indicating overpopulation compared with the equilibrium distribution. This corresponds to the early phases of excitation in Fig. 1. The surprisal becomes positive when the average internal energies are high, corresponding to the QSS region in Fig. 2 when the gas is rapidly dissociating. What is most interesting is that the surprisal is approximately linear over a wide range of internal energy levels (0.15 < εi/εd < 0.8). It is important to note from Fig. 2 that the population of molecules with εi/εd > 0.8 becomes vanishingly small, and therefore this portion of the distribution function has a limited effect on the overall system. The nonlinear nature at very high energies is a consequence of (i) when the average vibrational energy is low, the population of molecules in high-energy states becomes vanishingly small; and (ii) such high-energy vibrational states have strong rotation to rotational energy.

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constraint imposed by the dynamics of dissociation should be based on the translational energy of the system (relative to the dissociation energy, \( \epsilon_d \)). DMS results clearly show that as the system translational energy increases, the degree of internal energy depletion increases. At temperatures close to 10,000 K, depletion is limited to the high-energy tails; however, at higher temperatures, depletion occurs over a wider range of vibrational energy levels (15, 42).

The modeled nonequilibrium distribution function for vibration is then given by:

\[
 f(v) = C_{1,v} f_0(v) \exp\left[-\lambda_{1,v} \frac{\langle \epsilon_i \rangle}{\epsilon_d} v\right],
\]

where \( C_{1,v} = \exp[-\lambda_{0,v}] \) and can be obtained from the normalization condition, \( \sum_{v=0} \psi f(v) = 1 \).

Since rotational energy is approximately linear with \( j(j+1) \), as seen in Fig. 4, the surprisal is modeled as:

\[
 -\log \left[ \frac{f(j)}{f_0(j)} \right] = \lambda_{0,j} + \lambda_{1,j} \frac{\langle \epsilon_i \rangle}{\epsilon_d} j(j+1),
\]

where \( \lambda_{0,j} \) and \( \lambda_{1,j} \) are constants. The nonequilibrium distribution function for rotation is then:

\[
 f(j) = C_{1,j} f_0(j) \exp\left[-\lambda_{1,j} \frac{\langle \epsilon_i \rangle}{\epsilon_d} j(j+1)\right],
\]

where \( C_{1,j} = \exp[-\lambda_{0,j}] \), which can be evaluated by using the normalization condition, \( \sum_{j=0}^{\infty} f(j) = 1 \).

**Transient Distributions.** We now extend the above surprisal approach for OSS distributions to model the transient internal energy distributions during excitation.

Interestingly, as seen in Figs. 3 and 4, we find the surprisal to be approximately linear even during the transient phase. This motivates the formulation of a second constraint acting on the system that causes a deviation from equilibrium. As pointed out by Levine (48) (refer to Eq. 2), the surprisal with multiple constraints can be constructed as a linear combination of the constraints. During the excitation phase, the system will continue to evolve as long as the internal energy modes are not in equilibrium with the translational mode. Therefore, the average energy gap between these modes (in an antisymmetric manner) is proposed as the dynamical constraint. The resulting models for surprisal become:

\[
 -\log \left[ \frac{f(v)}{f_0(v)} \right] = \lambda_{0,v} + \lambda_{1,v} \frac{\langle \epsilon_i \rangle}{\epsilon_d} v + \lambda_{2,v} \left( \frac{2}{3} \frac{\langle \epsilon_i \rangle}{\epsilon_d} - \frac{3}{2} \frac{\langle \epsilon_i \rangle}{\epsilon_d} \right) v,
\]

and

\[
 -\log \left[ \frac{f(j)}{f_0(j)} \right] = \lambda_{0,j} + \lambda_{1,j} \frac{\langle \epsilon_i \rangle}{\epsilon_d} j(j+1)
 + \lambda_{2,j} \left( \frac{2}{3} \frac{\langle \epsilon_i \rangle}{\epsilon_d} - \frac{3}{2} \frac{\langle \epsilon_i \rangle}{\epsilon_d} \right) j(j+1),
\]

where \( \lambda_{2,v}, \lambda_{2,j}, \) and \( \psi \) (odd integer) are additional constants. Therefore, the final model for nonequilibrium internal energy distribution functions is:

\[
 f(i) = C_{1,i} f_0(i) \times \exp\left[-\lambda_{1,i} \frac{\langle \epsilon_i \rangle}{\epsilon_d} \Gamma_{i}\right]
 \times \exp\left[-\lambda_{2,i} \left( \frac{2}{3} \frac{\langle \epsilon_i \rangle}{\epsilon_d} - \frac{3}{2} \frac{\langle \epsilon_i \rangle}{\epsilon_d} \right) \psi \Gamma_{i}\right],
\]

where \( i \) corresponds to the internal mode \( (i \rightarrow v \) or \( j \)), \( \Gamma_v = v \), \( \Gamma_j = j(j+1) \), and \( f_0(i) \) is calculated by using Eq. 3 as previously described. Both population and depletion terms follow surprisal functions that are linear in \( v \), or \( j(j+1) \). In addition, the translation energy \( (\langle \epsilon_i \rangle/\epsilon_d) \) controls the depletion resulting from dissociation, whereas the energy gap \( (\langle \epsilon_i \rangle - \langle \epsilon_i \rangle) \) controls the overpopulation during rapid excitation. Given this physics-based functional form, the free parameters are then determined by comparison with baseline ab initio results obtained from DMS.

**Results and Discussion**

By using published DMS nonequilibrium distribution results (15, 33, 42), corresponding to nitrogen systems over a range of temperatures, the best-fit model parameter values were determined to be: \( \lambda_{1,v} = 0.080 \), \( \lambda_{2,v} = -7.3 \times 10^{-6} \), \( \lambda_{1,j} = 4.33 \times 10^{-4} \), \( \lambda_{2,j} = 1.00 \times 10^{-4} \), and \( \psi = 3 \).

Using our simplified model with these parameter values, we now compare with the results from DMS. Using only the average internal energy values, \( \langle \epsilon_{rot} \rangle, \langle \epsilon_v \rangle \), and \( \langle \epsilon_j \rangle \), at a specific time from DMS, we compare the corresponding nonequilibrium distributions from our simplified model with the actual distributions computed by DMS.

For the 20,000 K vibrational excitation distributions (Figs. 2 and 3), the model predictions are compared with DMS results in Fig. 5. The simple model captures the overpopulation of high \( v \) levels during excitation, when a large gap exists between \( \langle \epsilon_v \rangle \) and \( \langle \epsilon_j \rangle \). As the gas vibrationally excites and reaches a QSS, the degree of thermal nonequilibrium decreases, and the model predicts that the depletion of high \( v \) levels becomes the dominant term. The corresponding rotational energy distributions predicted by the model are compared with the DMS results in Fig. 6. The overall trends and level of agreement are similar to that found for vibrational energy.

Capturing such non-Boltzmann physics is important for modeling the flow behind strong shockwaves. Under certain hypersonic flight conditions, >50% of the gas dissociation in front of a spacecraft can occur in the transient excitation phase immediately behind the shockwave, with the remainder occurring in the QSS phase (16). Predicting the extent of dissociation in the shock layer surrounding a hypersonic vehicle is crucial for predicting thermal protection system (i.e., heat shield) performance. To first order, dissociation converts thermal energy into chemical energy through bond-breaking, which significantly lowers the shock-layer temperature and convective heating to the surface. At the same time, the production of reactive atomic species (such as N, but most importantly O) has a first-order effect on the
degradation of the heat shield material. Due to the strong coupling between vibrational energy and dissociation, even small changes in the vibrational energy distribution function (when viewed on a logarithmic scale) can result in noticeable changes in the overall extent of dissociation (15, 42).

**Continuum Modeling of Dissociation**

The integrated continuum dissociation rate coefficient \( k_d \) is determined by integrating \( p(d|e_s, i) \), the probability of dissociation given a particular state \( i \) and relative collision energy \( e_s \), over the distribution of relative energies and states. Without the integration constant, this expression has the following form (53):

\[
\sum_{\varepsilon_s > 0} \sum_{j=0}^{\infty} \int_{0}^{\infty} p(d|e_s, \varepsilon_{rot}, \varepsilon_v) f_0(\varepsilon_i) f(\varepsilon_{rot}) f(\varepsilon_v) d\varepsilon_s.
\]

When formulating continuum models, such integration is usually performed assuming equilibrium distributions, not only for the translational energy \( f_0(\varepsilon_i) \), but also for the internal energy distributions. However, the new model now enables integration over more accurate nonequilibrium internal energy distributions (Eq. 10), which capture key physics such as overpopulated and depleted high-energy tails.

In fact, if analytical expressions are used for \( f_0(v) \) and \( f_j(j) \), in place of Eq. 3, then we have shown that an analytical result can be obtained for the continuum rate coefficient (54), having the following form:

\[
k_d(T, \langle \varepsilon_{rot} \rangle, \langle \varepsilon_v \rangle) = AT^q \exp\left(\frac{-\varepsilon_{d}}{k_B T}\right) * G_{rot} * G_v.
\]

As an example, consider a continuum simulation solving for average energies, \( T, \langle \varepsilon_{rot} \rangle, \langle \varepsilon_v \rangle \), in the flow immediately behind a strong shockwave. The spatial evolution of internal energy and dissociation chemistry behind the shock would be analogous to the temporal evolution seen in Fig. 1. Consider the gas conditions at \( t \approx 2.9 \times 10^{-3} \) in Fig. 1, where \( T > \langle \varepsilon_{rot} \rangle >> \langle \varepsilon_v \rangle \). In this case, \( G_v \) would act to lower the Arrhenius rate expression since, although \( T \) is high, the gas is not vibrationally excited \((\langle \varepsilon_v \rangle \) is low), and dissociation should be delayed. Such an incubation period for dissociation behind strong shocks is an important effect that has been experimentally measured by Hornung and coworkers (55). However, although \( \langle \varepsilon_v \rangle \) is low, the high \( v \) levels are substantially overpopulated as seen in Fig. 2, and these high \( v \) levels will contribute to dissociation. Therefore, while some models may overpredict the dissociation rate by accounting only for \( T \), other models that account for only the average vibrational energy, \( \langle \varepsilon_v \rangle \), may predict virtually no dissociation. In contrast, the new model will predict a more accurate dissociation rate since it contains a representation of the underlying internal energy distribution functions.

Since the model is formulated in terms of average internal energies only, it can be incorporated into state-of-the-art computational fluid dynamics simulations (2) of nonequilibrium reacting flows.

**Conclusions**

To summarize, we propose a model for rotational and vibrational energy distributions, for gases in nonequilibrium, that enables coupling between internal energy and dissociation chemistry. Development of the model leverages recent advances in the construction of ab initio PESs for high-energy collisions in air (9, 10, 12, 13), as well as the recent capability to perform DMS of nonequilibrium gas systems by using only a PES (15, 40, 42). We find that a simple model, based on surprisal analysis, is able to predict the nonequilibrium internal energy distributions during rapid rovibrational excitation and dissociation of nitrogen gas. The surprisal-based model is able to accurately capture both the overpopulation of high-energy levels during the excitation phase, as well as the depletion of high-energy levels in the QSS dissociating phase. With an accurate representation of the underlying internal energy distributions, this enables state-specific reaction probabilities to be integrated over the new nonequilibrium distributions.
distributions (instead of integrating over equilibrium Boltzmann distributions). The result is an analytical continuum-level rate coefficient expression that contains information about the underlying nonequilibrium distributions of internal energy and their coupling to dissociation. The model was parametrized for nitrogen dissociation, but could potentially be parameterized for other gases and extended for modeling other systems where nonequilibrium coupling between internal energy and chemical reactions is important.

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