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Atomistic-level non-equilibrium model for chemically reactive systems based on steepest-entropy-ascent quantum thermodynamics

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Abstract. This paper outlines an atomistic-level framework for modeling the non-equilibrium behavior of chemically reactive systems. The framework called steepest-entropy-ascent quantum thermodynamics (SEA-QT) is based on the paradigm of intrinsic quantum thermodynamic (IQT), which is a theory that unifies quantum mechanics and thermodynamics into a single discipline with wide applications to the study of non-equilibrium phenomena at the atomistic level. SEA-QT is a novel approach for describing the state of chemically reactive systems as well as the kinetic and dynamic features of the reaction process without any assumptions of near-equilibrium states or weak-interactions with a reservoir or bath. Entropy generation is the basis of the dissipation which takes place internal to the system and is, thus, the driving force of the chemical reaction(s). The SEA-QT non-equilibrium model is able to provide detailed information during the reaction process, providing a picture of the changes occurring in key thermodynamic properties (e.g., the instantaneous species concentrations, entropy and entropy generation, reaction coordinate, chemical affinities, reaction rate, etc). As an illustration, the SEA-QT framework is applied to an atomistic-level chemically reactive system governed by the reaction mechanism $F + H_2 \Leftrightarrow FH + H$.

1. Introduction

Studying the kinetics and dynamics of an atomistic-level system is a central topic of interest in physics and thermodynamics. Classical mechanics and quantum mechanics, which are built on Newton's and Schrödinger's equations of motion, respectively, provide an almost perfect description of the zero-entropy phenomena occurring in nature. However, both lack the 2nd law of thermodynamics and are, thus, unable to provide a description of states at stable equilibrium with non-zero values of the entropy. To do so, both statistical thermodynamics (ST) and intrinsic quantum thermodynamics (IQT) use principles derived from the 2nd law, namely, the maximum entropy and minimum energy principles, to arrive in constrained optimizations at a description of such states. However, this still leaves a gap not described between the zero-entropy and the maximum-entropy worlds, a gap which is important for a complete understanding of system

behavior since it contains information about the kinetics and dynamics of non-equilibrium, non-zero-entropy, system-state evolutions. To fill this gap, IQT [1-29] has emerged over the last several decades as a theory which unifies quantum mechanics and thermodynamics and provides a complete picture of the kinetics and dynamics of system behavior in this region [25].

Of course, underlying any such description is the 2nd law of thermodynamics and the dissipative phenomena which occur in a realm where the beautiful symmetry of the time reversibility of classical mechanics and quantum mechanics and that of the quasi-equilibrium processes of classical thermodynamics is broken. A traditional way of studying the state evolutions in this region is that of quantum thermodynamics (QT) [30,31], which discards the isolation of the system, forming a so-called "open-system" model that includes "weak-interactions" with the environment. This approach places the system into a larger composite of system plus environment so that the dynamics of the dissipative phenomena present can be modeled as linear in the near-equilibrium realm of the composite. Thus, the QT master equations of the Lindblad type [32-35] retain the linear and reversible characteristics of the Schrödinger equation of motion, viewing dissipative phenomena as effects external to the system. This limits, among other things, this theory to the near-equilibrium and weak-interaction regimes and eschews entropy and entropy generation as intrinsic to the system.

In contrast, IQT regards the entropy and entropy generation as intrinsic and directly incorporates the irreversible and non-linear features of the dissipative process into the theory and its equation of motion. In this way, IQT avoids the necessity of introducing an external environment and does not limit itself to the near-equilibrium realm of weak system-environment interactions. Furthermore, in the limit of time reversibility, the IQT equation of motion reduces to the linear Schrödinger-von Neumann equation of quantum mechanics, which describes the linear dynamics of zero-entropy-state evolutions.

Now, of all the non-equilibrium phenomena of interest, those of chemically reactive systems are some of the most frequently studied in science and engineering. Starting with the Van't Hoff-Arrhenius law [36,37], the study of the kinetics and dynamics of chemical reactions remains an important topic of theoretical chemistry even today [38,39]. The result is a set of theories which attempt to explain the mechanisms of chemical reactions and to predict their properties using classical mechanics or quantum mechanics or a mix of both.

Conventional theory describes the kinetic features of a reactive system using configuration space (or phase space), while potential energy surfaces (PESs) serve as constraints in configuration space. In this space, the chemical reaction is regarded as a motion from the reactant region to the product region, and the kinetics are represented by a path found, for example, via the Minimum Energy Principle [40] or by a group of possible trajectories [41,42] on the PES. The associated dynamics of each reaction mechanism is then viewed as resulting from inelastic collisions [43] and the motions of single particles for which temperature plays an important role [44]. In contrast, the kinetics of each reaction mechanism provides the 'environment' for particle motion and contributes to the important concepts of potential energy barrier [45] and activated complex (e.g, in Transition State Theory) [46,47], which underlie the exponential term in the Van't Hoff-Arrhenius law. With the microscopic velocities and a reaction path or set of trajectories known, a reaction rate calculation can be made via the kinetics in configuration space. Taking into account the uncertainty in the position or momentum of each particle, an ensemble of reactant particles resulting in a Maxwellian velocity distribution can be used to arrive at reasonable expectation values for reactant concentrations, which in turn provides a link to the statistical thermodynamic value of the entropy. Of course, quantum theory can be used to modify and improve, for example, the classical calculations [45] of the PES in order to include important quantum effects such as tunneling and the discrete nature of the energy spectrum of each particle. These so-called quasi-classical calculations can then be further improved by replacing them with a fully quantum calculation using quantum scattering theory based on either the time-dependent or time-independent Schrödinger equation [48,49].

These conventional theories, whether classical, quasi-classical, or quantum, suffer from two disadvantages. First, both temperature and the Maxwellian velocity distribution play an important role in the theories but are valid only at stable equilibrium. The problem with this is that stable equilibrium only exists at the end of the reaction process whereas all prior states are in non-equilibrium, possibly very far from equilibrium. Second, the chemical reaction process in these theories is described by motion in configuration or phase space and the evolution of particle position and momentum is the principal driving force for the chemical reaction. This evolution is determined using an equation of motion which classically is given by Hamilton's equations or quantum mechanically by Schrödinger's equation. Either is reversible and, thus, there is the inevitable contradiction of using a reversible equation of motion to describe what inherently is an irreversible process. This compromise is made since the theories lack an equation of motion at a fundamental level of description for dissipative processes. Of course, turning at a classical level to the Boltzmann equation of motion, which only provides a phenomenological description, or at the quantum level to QT and its master equations of the Lindblad type, which do provide a fundamental description, only begs the question since both suffer from the so-called Loschmidt paradox [50] of how an underlying dynamics, which for both is reversible or unitary, can lead to an irreversible result.

These two essential weaknesses are addressed in IQT and its mathematical framework steepest-entropy-ascent quantum thermodynamics (SEA-QT). To begin with, the SEA-QT framework links the zero-entropy and maximum entropy worlds by providing a comprehensive description of the non-equilibrium states of the system. Entropy, which is universally defined and intrinsic to the system, is used instead of temperature to provide information for the microscopic description. All the necessary information for system state evolution is derived from the energy eigenstructure and entropy of the system via the non-linear SEA-QT equation of motion. Furthermore, the irreversibility of the chemical reaction is no longer regarded as a phenomenon resulting from particle collisions and the movement of single microscopic particles although both can be present and taken into account but instead as a dissipative process derived from the principle of steepest entropy ascent (SEA) or local maximal entropy generation (LMEG), which is a macroscopic or group effect at a fundamental level of description. Second, the SEA-QT framework describes the system in a state space spanned by eigenstates of the reactants and products and not in a configuration or phase space. Recalling that quantum effects are very important at the atomistic level, the use of state space has the advantage of directly representing the uncertain position and momentum of each energy eigenstate. Furthermore, the energy eigenstructure, which is a fundamental feature of the system, is described by eigenlevels of the system Hamiltonian and does not require the very time consuming calculation of a PES and of particle or wave packet trajectories on the PES (also very time consuming).

With these advantages in mind, the SEA-QT framework is applied here to the well-studied chemical reaction mechanism $F + H_2 \Leftrightarrow FH + H$. A system using a finite number of energy eigenlevels as its energy eigenstructure is used and compared with one based on an infinite number of energy eignlevels. In Section 2, the mathematics for expressing system states in state space is described and the energy eignstructure of the system is built from single particle eigenstates. The SEA-QT equation of motion is then presented and briefly discussed. In Section 3, results are presented which demonstrate the crucial role that entropy plays in dissipation phenomena. Results for the chemical reaction path and reaction rate are also presented and linked to experimental data. The chemical kinetic results for the finite-level system are then compared to those for the infinite-level system. Section 4 provides some further discussion and conclusions.

2. Method

2.1 State description

The description of state of a chemically reactive system is at the core of the SEQ-QT framework [24,28,29]. The SEA-QT description is based on an algebraic representation, which is quite different from the conventional description in configuration space (e.g., as in Transition State Theory) or the wave packet description using multi-body eigenfunctions (e.g., as in the Quantum Scattering Method). This avoids having to express particle position and momentum under conditions of uncertainty and brings to the fore the energy and entropy as being of primary significance. Thus, the kinetics and dynamics in the SEA-QT framework depend principally on the critical concepts of energy and entropy for defining coordinates in state space and not on momentum and position as in phase space or configuration space. This provides a clearer vantage point from which to see the driving role, which entropy plays in the non-equilibrium evolutions of state of chemically reactive systems. The behavior in phase space or configuration space, which is not fundamental but which is extremely complex, is simply another view of system state evolution.

The state space of the chemically reactive system is spanned by the eigenstates of the reactants and those of the products. Intermediate states between reactants and products are represented by a mixture of reactant states and product states. This state space can be represented by the Hilbert space $\mathscr{H}$ as follows:

$$\mathscr{H} = \mathscr{H}_1 \oplus \mathscr{H}_2 \tag{1}$$

where $\mathscr{H}_1$ is the subspace of reactants and $\mathscr{H}_2$ is the subspace of products. Each subspace of the state is generated from single molecular state spaces by the cross product. In this paper, the reaction

$$F + H_2 \Leftrightarrow FH + H \tag{2}$$

is modeled so that each subspace is given by

$$\mathscr{H}_1 = \mathscr{H}_{H_2} \oplus \mathscr{H}_F \tag{3}$$

$$\mathscr{H}_2 = \mathscr{H}_{FH} \oplus \mathscr{H}_H \tag{4}$$

The eigenstate of each molecule is generated from the one-particle eigenstates available to each molecule. For example, the state space of H_2 is expanded to include degrees of freedom for translation, rotation, vibration such that

$$\mathscr{H}_{H_2} = span\left\{ \left| t_x t_y t_z \right\rangle_{H_2} \otimes \left| lm \right\rangle_{H_2} \otimes \left| v \right\rangle_{H_2} \right\} \tag{5}$$

where $\left| t_x t_y t_z \right\rangle$ represents the translational eigenstates, $\left| lm \right\rangle$ the rotational ones, and $\left| v \right\rangle$ the vibrational ones. Inside each *ket* are the quantum numbers for the one-particle eigenstate.

Starting from the one-particle eigenstates, one can represent the system-level eigenstate $\left| \vec{n} \right\rangle$ of the reactants or products by a quantum number group composed of translational, rotational, and vibrational one-particle eigenstates, i.e.,

$$\left| \vec{n} \right\rangle = \left| 1(t_x t_y t_z lmv)_{H_2} (t_x t_y t_z)_F \right\rangle \qquad \text{for the reactants} \tag{6}$$

$$\left| \vec{n} \right\rangle = \left| 2(t_x t_y t_z lmv)_{FH} (t_x t_y t_z)_H \right\rangle \qquad \text{for the products} \tag{7}$$

In Eqs. (6) and (7), each eigenstate for the reaction mechanism of Eq. (2) of the chemically reactive system is represented by a total of 10 indices. The first refers to the subspace (1 or 2), 6 to the quantum numbers for the diatomic molecules H_2 and FH, and 3 to the quantum numbers for the monatomic molecules H and F. The thermodynamic state of the system can then be written in a superposition of system eigenstates such that

$$\left| \Psi \right\rangle = \sum_{\vec{n}} \gamma(\vec{n}) \left| \vec{n} \right\rangle \tag{8}$$

where $\gamma(\vec{n}) = \sqrt{p(\vec{n})}$ is the square root of the probability $p(\vec{n})$ of system energy eigenlevel $|\vec{n}\rangle$. Given the energy eigenstructure of the system, the system's thermodynamic state can also be represented by the probability distribution $p(\vec{k})$ where the $\vec{k}$ are all of the possible quantum number groups of $|\vec{n}\rangle$.

2.2 Energy eigenstructure

As developed in [24] for chemically reactive systems, the Hamiltonian and identity operators are the generators of motion in the kinetics and dynamics of the SEA-QT framework. In addition, the state of the system is represented by a probability distribution of available energy eigenlevels. The evolution of system state results in a different distribution for each state at every instant of time. Thus, generating the system-level energy eigenstructure of available levels for the chemically reactive system is an important step in the development of the SEA-QT model for the system. This system-level structure is constructed from sets of one-particle eigenlevels, which for the reactive systems based on Eq. (1) considered here consist of the translational energies of the center of mass (ε_t), rotational energies (ε_r), and vibrational energies (ε_v). For F and H, which lack an internal structure, only translational energies need be considered. For translation,

$$\varepsilon_t(t_x,t_y,t_z) = \frac{\hbar^2}{8m}\left(\left(\frac{t_x}{L_x}\right)^2 + \left(\frac{t_y}{L_y}\right)^2 + \left(\frac{t_z}{L_z}\right)^2\right) \qquad (9)$$

where ε_t is the one-particle translational energy eigenvalue; $\hbar$ Plank's modified constant; m the center of mass of the particle; (t_x,t_y,t_z) the quantum numbers in the x, y, and z directions; and (L_x,L_y,L_z) the dimensions of system volume in the x, y, and z directions.

For the internal structure of the diatomic molecules H_2 and FH, the one-particle rotational energy eigenvalue is given by

$$\varepsilon_r(l,m) = \frac{J(J+1)\,\hbar^2}{2\mu r^2} \qquad (10)$$

where μ the reduced mass of the diatomic molecule, r the distance between the two atoms of the diatomic molecule, l the azimuthal quantum number, and m the magnetic quantum number. For vibration, the one-particle energy eigenvalue from the oscillator potential is written as

$$\varepsilon_v(v) = (v + \tfrac{1}{2})\hbar\omega \qquad (11)$$

where ω is the angular frequency of the potential and v the quantum number for vibration.

The system-level energy eigenvalues for each subspace can now be found from

$$E_{\vec{n}} = E\left(\left|1(t_xt_yt_zlmv)_{H_2}(t_xt_yt_z)_F\right\rangle\right)$$
$$= \varepsilon_{t,H_2}(t_x,t_y,t_z) + \varepsilon_{t,F}(t_x,t_y,t_z) + \varepsilon_{r,H_2}(l,m) + \varepsilon_{v,H_2}(v) \qquad (12)$$

for subspace 1 and from

$$E_{\vec{n}} = E\left(\left|2(t_xt_yt_zlmv)_{H_2}(t_xt_yt_z)_F\right\rangle\right)$$
$$= \varepsilon_{t,FH}(t_x,t_y,t_z) + \varepsilon_{t,H}(t_x,t_y,t_z) + \varepsilon_{r,FH}(l,m) + \varepsilon_{v,FH}(v) \qquad (13)$$

for subspace 2. Combining these values from the two subspaces results in the system energy eigenstructure.

2.3 Property Operators

In quantum mechanics, an observable is represented by a single Hermitian operator. In a like manner, the SEA-QT framework is written in terms of operators. To begin with, the density operator of the system is given by

$$\rho = \sum_{\vec{n}} p(\vec{n}) P_{\vec{n}} \tag{14}$$

where $P_{\vec{n}}$ is the projector of a given eigenstate $/\vec{n}\rangle$ of the system expressed as

$$P_{\vec{n}} = |\vec{n}\rangle\langle\vec{n}| \tag{15}$$

Since $P_{\vec{n}}$ is the basis in operator space, all other operators can be written as a superposition of the projector. Thus, the particle number operators are given by

$$N_{H_2} = N_F = \sum_{\substack{\vec{n} \text{ of} \\ \text{reactant}}} |\vec{n}\rangle\langle\vec{n}| \tag{16}$$

$$N_{FH} = N_H = \sum_{\substack{\vec{n} \text{ of} \\ \text{product}}} |\vec{n}\rangle\langle\vec{n}| \tag{17}$$

while the Hamiltonian operator is expressed as

$$H = \sum_{\vec{n}} E_{\vec{n}} |\vec{n}\rangle\langle\vec{n}| \tag{18}$$

As to the reaction coordinate and reaction rate operators for the system considered here, they are written as

$$\varepsilon = N_{FH} \tag{19}$$

$$r = \frac{dN_{FH}}{dt} \tag{20}$$

Of course, the SEA-QT framework as presented above provides only a very brief outline of the overall framework. A more general and comprehensive treatment can be found in Beretta and von Spakovsky [24] as well as in Al-Abbasi [29].

Finally, for any observable *A*, its expectation value can be calculated at any given instant of time by

$$\langle A \rangle = Tr(\rho A) \tag{21}$$

since $\rho = \rho(t)$ is known via the SEA-QT equation of motion. Here $Tr(\cdot)$ is the trace of the operator. Eq. (21) is equally applicable for the observables of finite- and infinite-level systems with the exception of the entropy for which the expectation value for a finite-level system in a state of non-equilibrium is determined from

$$\langle S \rangle = -k_B Tr(\rho \ln \rho) \tag{22}$$

Here k_B is the Boltzmann constant. For an infinite-level system in a non-equilibrium state, however, Eq. (22) must be modified as explained in the following section.

2.4 Density of State Method

To deal with an infinite-level system in the non-equilibrium realm, the expression for the expectation value of the entropy is modified using the density of states method developed by the first and third authors. The details of this method will be reported in a future paper, which is now

in preparation. The same approach can be used for a continuous energy eigenspectrum system as well as a degenerate system. Using this method, the energy eigenstructure can be approximated by a degenerate group of sampled energy eigenlevels where the degeneracy is proportional to the density of state of each sample energy value. As will be shown in a future paper, a set of energy eigenlevels in a small interval can be approximated by one energy value with degeneracy to an accuracy on the order of the length of the interval. With this modification, each degenerate energy value is equivalent to the set of energy eigenlevels for a given interval and contributes to the SEA-QT equation of motion and the modified system entropy, i.e.,

$$\langle S \rangle = -k_B Tr\left(\rho\, ln\, \frac{\rho}{N(\vec{n})} \right) \qquad (23)$$

with the same kinetics and dynamics that would be present if all the infinite number of energy eigenlevels were explicitly taken into account. Note that $N(\vec{n})$ is the degeneracy for energy level $|\vec{n}\rangle$.

2.5 SEA-QT equation of motion
The SEA-QT equation of motion is presented directly here without derivation. For details of the derivation, the reader is referred to [18,24,29]. The equation of motion for a reactive system is written here in operator form and is expressed as

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H,\rho] + \frac{1}{2k_B\tau}\{\Delta M, \rho\} \qquad (24)$$

where the first term on the right captures the linear Hamiltonian dynamics and the second the non-linear dissipative dynamics. When the system is in a zero-entropy state, the second term vanishes, and the SEA-QT equation of motion reduces to the time-dependent Schrödinger-von Neumann equation. In the dissipative term, τ is a relaxation time, which is the characteristic time of the dissipation process and can either be a constant or a function of ρ. {} is the anti-commutator operator, while $\Delta M = M - \langle M \rangle$ is the deviation from the mean of the non-equilibrium Massieu operator defined as $M = S - H/\theta_H$ where $\theta_H = \langle \Delta H \Delta H \rangle / \langle \Delta S \Delta H \rangle$ is a constant-energy, non-equilibrium temperature and S and H are the entropy and Hamiltonian operators, respectively.

2.6 Initial state generation
To generate an initial density or state operator $\rho^{in}(\vec{n})$ for the SEA-QT equation of motion, the following procedure is used. It is assumed that the reactants are a Gibbs-Dalton mixture of ideal gases in an isolated container. Initially, the mixture is in a state of stable equilibrium of a non-reactive system at some temperature T. The mixture is then ignited to move the state of the system into a state of non-equilibrium at which point the system becomes chemically reactive. The physical meaning of such a system can be that of a reactive system that requires ignition or a system whose reaction speed is much smaller than its diffusion speed. The initial canonical or stable equilibrium distribution $\rho^{se}(\vec{n})$ in reactant subspace at temperature T can be represented by

$$\rho^{se}(\vec{n}) = \frac{e^{-\beta E_{\vec{n}}}}{\sum e^{-\beta E_{\vec{k}}}} \qquad \text{for } \vec{n} \text{ and } \vec{k} \text{ in the reactant subspace} \qquad (25)$$

where $\beta = 1/k_B T$. Initially, this distribution is that of the system as a whole as well since only reactants are present. The ignition process is described by a perturbation of this canonical distribution $\rho^{se}(\vec{n})$ in both the reactant and product subspaces such that

$$\rho^{in}(\vec{n}) = \frac{(1-\delta)e^{-\beta E_{\vec{n}}}}{\sum e^{-\beta E_{\vec{k}}}} \qquad \text{for } \vec{n} \text{ and } \vec{k} \text{ in the reactant subspace} \qquad (26)$$

$$\rho^{in}(\vec{n}) = \frac{\delta e^{-\beta E_{\vec{n}}}}{\sum e^{-\beta E_{\vec{k}}}} \qquad \text{for } \vec{n} \text{ and } \vec{k} \text{ in the product subspace} \qquad (27)$$

where δ is a very small number.

2.7 Numerical approach
Since the number of system energy eigenlevels is extremely large, a finite number from all possible $|\vec{n}\rangle$ is chosen for the finite-level system model. This finite number is sufficient to describe the entropy-driven phenomena of the reactive system and link the predicted results with published experimental data. The energy eigenlevels chosen are listed in Table 1. For the infinite-level system, the density of state method briefly described above in Section 2.4 is used. The kinetics for both systems is the same. Differences in results manifest themselves in the dynamics with the latter system, of course, more closely representing the actual reactive system.

As to the equation of motion, it is solved here using a fourth order Runge-Kutta explicit scheme [51-53] with the relative tolerance error set to 1e-5.

Table 1. Quantum numbers considered for each of the molecules and atoms in the SEA-QT model [28,29].

Species	Translational quantum nos.[a]	Vibrational quantum nos.	Rotational quantum nos.
F	$t=1,...,5500$		
H_2	$t=1,...,1000$	$v=0$	$J=0,1,2,3$
FH	$t=1,...,1000$	$v=0,1,2,3,4$	$J=0,1,...,10$
H	$t=1,...,5000$		

[a] Although the translational principal quantum number *t (defined as the square root of* $t_x^2 + t_y^2 + t_z^2$*)* varies here in the range shown in the second column of the table for each species, only a sampling (10) of these quantum numbers across this range is used for each species in the SEA-QT model.

3. Results

3.1 Entropy and concentration evolution
The SEA-QT chemical reaction model is based on the idea that the entropy generation via the principle of steepest entropy ascent is the driving force behind the chemical reaction. The first reactive system considered here initially consists of 1 mol of H_2 and 1 mol of F contained in a cubic tank, 10 cm on a side. For this system, only the infinite-level model based on our density of state method is used.

Figure 1 shows the evolution in time of the expectation values of the entropy and the particle number. It is evident that the expectation values of the species particle numbers evolve in a fashion similar to that of the entropy and that this is consistent with the idea that the entropy generation is the driving force of the chemical reaction. The entropy is, thus, not simply a phenomenological property calculated to check whether or not a system behaves consistently with the 2nd law of thermodynamics but instead a means for applying the 2nd law to the description and prediction of the non-equilibrium kinetics and dynamics of chemically reactive systems. In addition, note that Figure 1b verifies that the mass of the system is conserved at every instant of time throughout the evolution of state of the system. Although not shown here, similar graphs for the expectation values

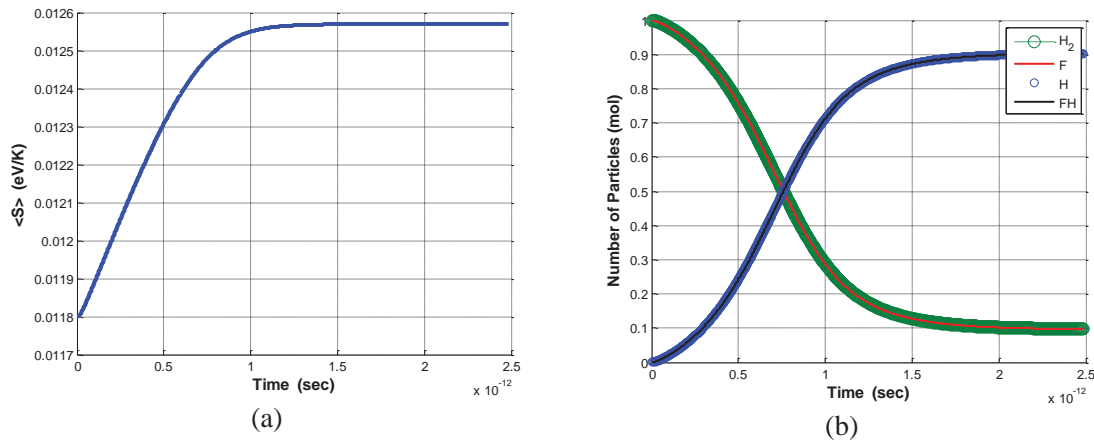of the energies of the species show that energy is also conserved at every instant of time throughout the evolution.

Figure 1. Evolution of the expectation values of system (a) entropy and (b) species particle number for the infinite energy eigenlevel system initially at a temperature of 298 K.

3.2 Chemical reaction rate
Solution of SEA-QT equation of motion provides system information at every instant of time, which can be used to calculate the chemical reaction rate. The traditional reaction rate constant $k(T)$ or thermal rate constant reported in the literature is a function of the initial stable equilibrium temperature of the reactive system and is a single value for each temperature, i.e., it does not vary in time during the reaction since it is a value gleamed from the initial reaction rate. In contrast, the SEA-QT framework is able to predict the reaction rate constant at every instant of time independent of temperature, referencing this temperature only in a post-processing procedure which allows the SEA-QT results to be compared to those in the literature. The SEA-QT framework is, thus, consistent with the fact that the chemical reaction process is a non-equilibrium process for which no temperature is defined. Moreover, the state of a chemically reactive system varies a lot not only with respect to the species concentrations but as well with respect to the entropy generation. The SEA-QT framework, therefore, provides a more complete picture of all the intermediate states of the system and the instantaneous chemical reaction rates in the non-equilibrium region.

Now, for the reaction mechanism considered here, i.e., $F + H_2 \Leftrightarrow FH + H$, the reaction rate is given by

$$r(t) = r_f(t) - r_b(t) \tag{27}$$

$$r_f(t) = k_f [F(t)][H_2(t)] \tag{28}$$

$$r_b(t) = k_b [FH(t)][H(t)] \tag{29}$$

where r is the net reaction rate, r_f the forward reaction rate, and r_b the backward reaction rate. k_f and k_b are the forward and backward reaction rate "constants", while $[A(t)]$ is the concentration of species A, which can be found from its particle number expectation value and the geometric dimensions of the system. The reaction order for each species in the reaction coincides here with the stoichiometric coefficient of each species in the reaction mechanism. However, this is not generally the case [54].

At stable equilibrium, Eqs. (27) to (29) provide a zero rate condition. With this condition and the assumption that the detailed balance condition also holds for the time-dependent rate constant, another relation is found, i.e.,

$$\frac{k_f(t)}{k_b(t)} = \frac{k_f(t^{se})}{k_b(t^{se})} = \frac{[F(t^{se})][H_2(t^{se})]}{[FH(t^{se})][H(t^{se})]} \tag{30}$$

which can be used with Eqs. (27) to (29) to calculate the $k_f(t)$ and $k_b(t)$ at every instant of time. In this last equation, t^{se} is the time at stable equilibrium.

The reaction rate constant values provided in the literature are those for the forward reaction at the beginning of the reaction process when the backward reaction is negligible. To make a comparison with the experimental data found in Heidner *et al.* [55], initial values for $k_f(t = t_0) = k_f(T^{in})$ for different initial equilibrium temperatures are calculated with the SEA-QT equation of motion by adjusting the relaxation time τ in the equation of motion to match the experimental data. The results for the infinite-level system are presented in Table 2, which lists the relaxation time calculated from the experimental data and the T^{eq}. The latter are the final stable equilibrium temperatures of the system corresponding to each initial stable equilibrium temperature. Of course, it is important to point out that the kinetic path of the chemical reaction process predicted by the SEA-QT framework is independent of the speed of system state evolution, i.e., of the relaxation time. No matter which relaxation time we use, the non-equilibrium path in state space remains the same. This result can be shown from the equation of motion where the relaxation time does not influence the relative value of each probability. We fit the relaxation time with the experimental data in order to show our state-space path result in the proper time scale.

Table 2. Equilibrium temperatures and relaxation times of the SEA-QT infinite-level model matched to the experimental values of the reaction rate constants found in Heidner *et al.* [55].

T^{in}(K)	T^{eq}(K)	$k_f(T^{in})/10^{-11}$ (cm^3/molecule-sec) [55]	$\tau/10^{-14}$ (sec)
298	3906.84	2.93	15.3045
400	3981.67	4.88	7.4923
500	4054.37	6.57	4.7362
600	4126.64	8.01	3.4038
700	4198.57	9.23	2.6453

Figure 2 shows a typical temperature evolution for the chemically reactive system. As mentioned above, intermediate states are non-equilibrium states for which the temperature is not defined. Nonetheless, using the surrogate system approach outlined in [29], a stable equilibrium temperature can be associated with each of these system states by using the entropy of each intermediate state at a given system energy and the fundamental relation for the entropy of a Gibbs-Dalton mixture of ideal gases to solve for the corresponding equilibrium temperature. For the infinite-level system, this temperature can also be gleamed from the slope of the curve of stable equilibrium states in the energy-entropy plane corresponding to the surrogate system [29] associated with a given intermediate (i.e., non-equilibrium) state at given values of the energy and entropy.

In Figure 3a, the characteristics of the reaction rates in the non-equilibrium realm for the infinite-level system are presented. The rates show a behaviour similar to that for the entropy generation rate, which puts in evidence once more the idea that the chemical reaction is driven by the entropy generation. The evolutions of the forward and backward reaction rates are consistent with what would be expected for a chemical reaction, namely, that the forward reaction rate dominates initially and then begins to diminish its dominance over the backward rate as the reaction proceeds until both cancel each other at stable equilibrium consistent with the initial detailed balance assumption.

Finally, Figure 3b shows an extension of the conventional reaction rate "constant" to one that has a different value at every instant of time. This more complete description of the reaction process has a clear physical meaning, namely, that the evolving state of the system in a dissipative process

results in varying reaction speeds. This is consistent with the temperature evolution shown in Figure 2, i.e., that the rapid rate of increase in temperature seen initially coincides with the rapid increase in the net reaction rate after which it slows as the net reaction rate decreases.
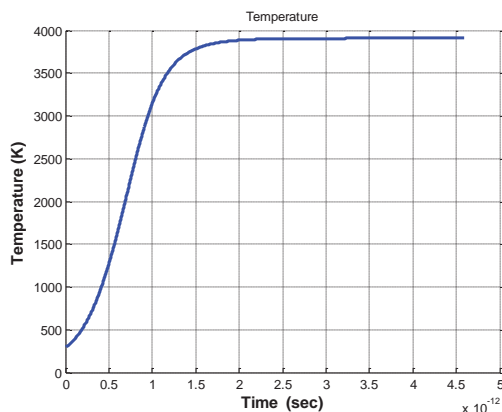

Figure 2. Evolution of temperature for the infinite-level system initially at a temperature of 298 K.
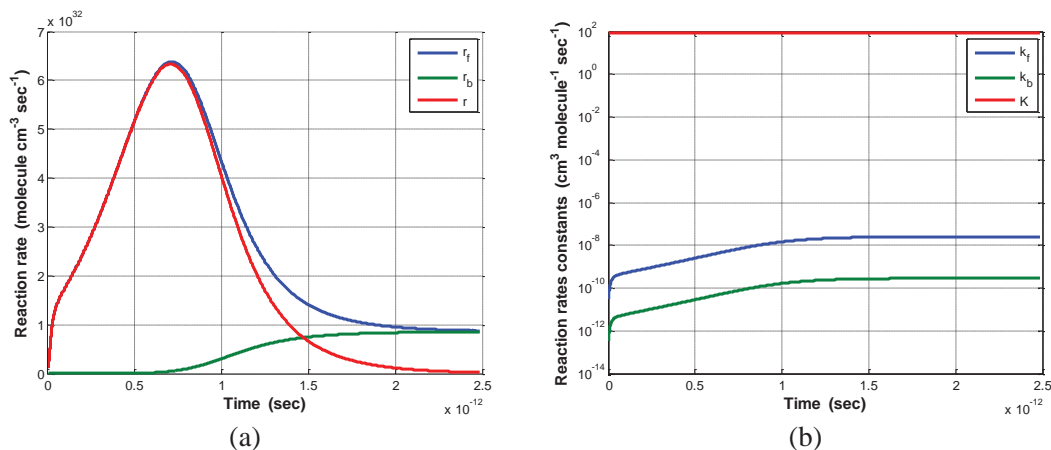

Figure 3. (a) Chemical reaction rates and (b) reaction rate constants for the infinite-level system initially at a temperature of 298 K.

3.3 Comparison of infinite-level model and finite-level model

Use of the density of states approach that we have developed has allowed us to extend the finite-level system approach reported in [24,28,29] from the microscale to the macroscale. However, to demonstrate the improvement of the infinite-level model results over that for the finite-level model at the microscale, the number of particles considered and the size of the system are reduced to one particle of H_2 and one of F in a tank with dimensions 4 nm by 2 nm by 2 nm. Anything larger results in computational convergence problems with the finite-level system model.

Figures 4 and 5 show the evolution in time of the expectation values of the entropy and entropy generation rate for the finite- and infinite-level systems. A number of differences can be seen. The first is that the maximum entropy value and the entropy generation peak value for the finite-level system are, respectively, a little less than one and a little greater than one order of magnitude smaller than that for the infinite-level system. In contrast, the evolution time to stable equilibrium for the infinite-level system is about half an order of magnitude smaller than that for the finite-level system. In addition, although the shapes of the entropy generation rate curves are similar for the two systems, that for the latter is much more asymmetric with a wider peak than that for the former

suggesting that the irreversible phenomena present differ much more in intensity throughout the evolution in state of the latter system.
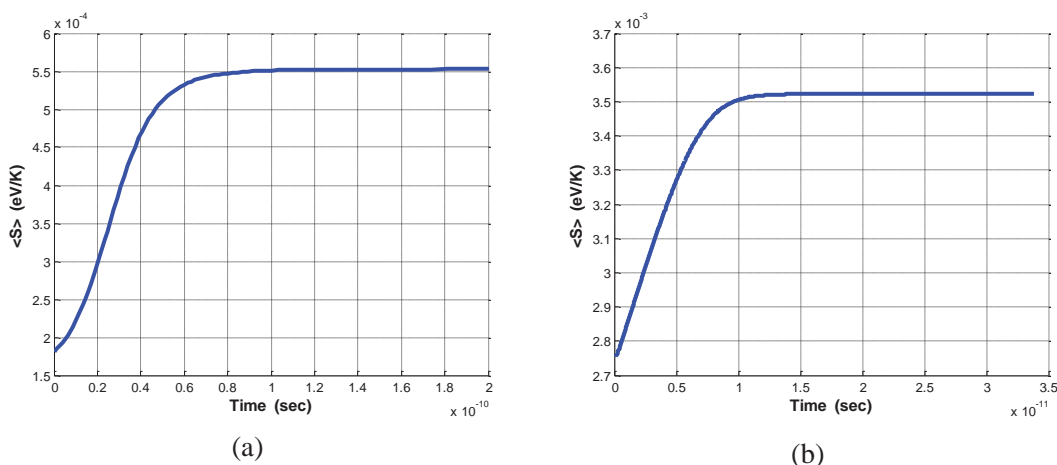

Figure 4. Evolution of the expectation values of system entropy for (a) the finite energy eigenlevel system and (b) the infinite energy eigenlevel system initially at a temperature of 298 K.
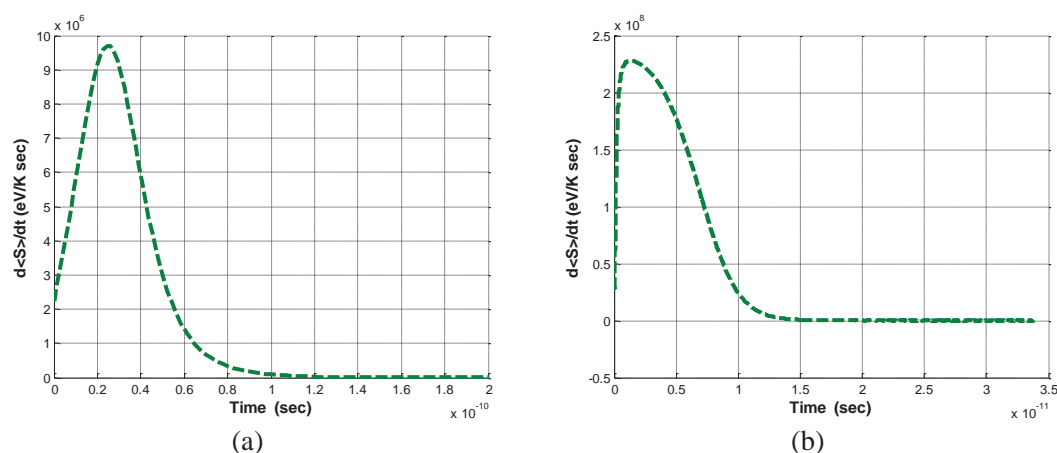

Figure 5. Entropy generation for (a) the finite energy eigenlevel system and (b) the infinite energy eigenlevel system initially at a temperature of 298 K.

Clearly, for a fixed system energy, the more energy eigenlevels available over which the energy can be distributed, the higher the system entropy. In fact, using the infinite-level model, one can validate the SEA-QT model prediction of the expectation value of the entropy at stable equilibrium by comparing it with that found from standard calculations using the maximum entropy principle of ST or IQT. Indeed good agreement is seen. Similarly, the larger the number of energy eigenlevels available, the larger the entropy generation is expected to be and the faster the dynamics. Again, this is indeed what is observed.

Finally, Figures 6 and 7 show the reaction rates and reaction rate constants for the finite- and infinite-level systems, respectively. Clearly, as seen in Figure 6, the peak reaction rates for the latter system are about half an order of magnitude large than those for the former, which explains the order of magnitude reduction in the evolution time for the latter seen here and in previous figures. As expected, the trends are comparable to those seen for the entropy generation rates in Figure 5. The differences in the reaction rate constants k_f and k_b seen in Figure 7 are, on the other hand, more

pronounced, showing a difference of two orders of magnitude between the k_f and k_b for each system model as well as differences of as much as one order of magnitude between the finite- and infinite-level systems even though the initial forward reaction rate constant k_f for both is set to be the same.
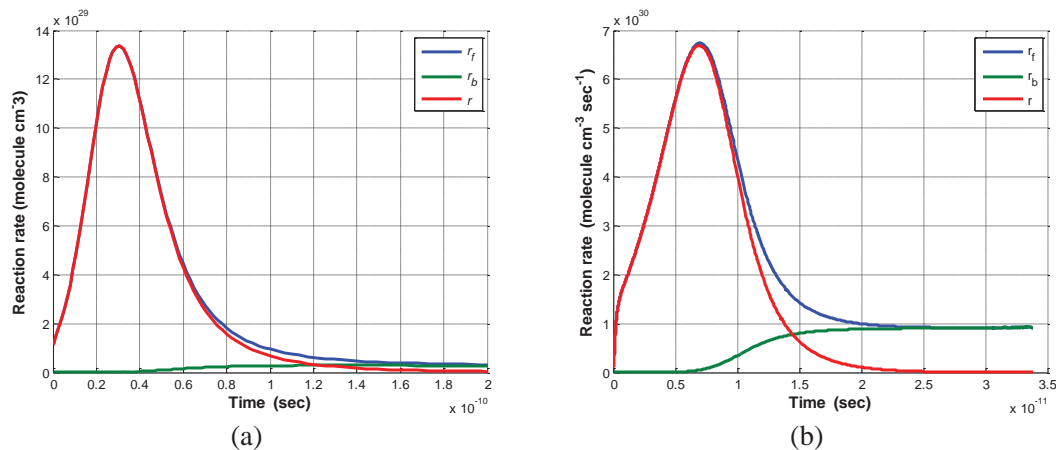

Figure 6. Chemical reaction rates for (a) the finite energy eigenlevel system and (b) the infinite energy eigenlevel system initially at a temperature of 298 K.
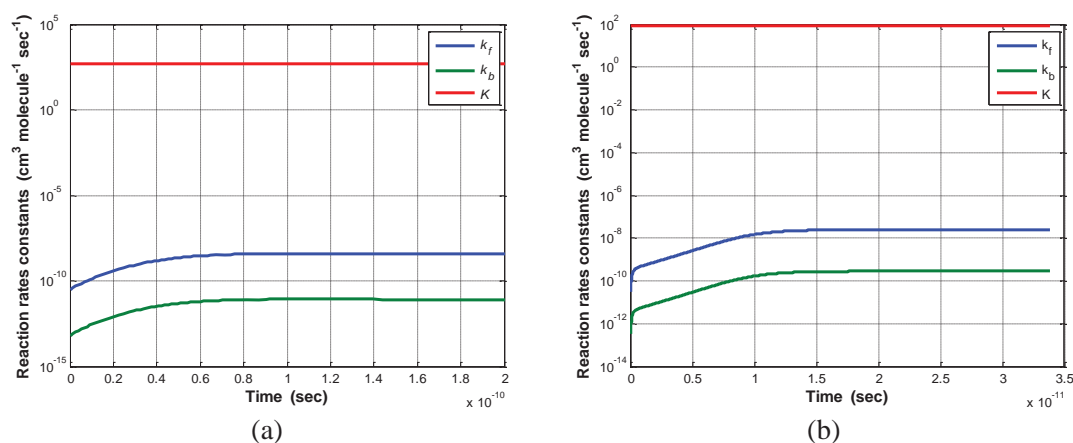

Figure 7. Reaction rate constant for (a) the finite energy eigenlevel system and (b) the infinite energy eigenlevel system initially at a temperature of 298 K.

4. Conclusions

The SEA-IQT chemical reaction framework provides a new fundamental approach to studying chemically reactive systems, especially their non-equilibrium behaviour. A major benefit of this framework is that it accounts for both the quantum mechanical and thermodynamic features of the system and the process it undergoes. It is different from conventional state-to-state chemical reaction models in that it uses the system energy eigenstructure and a non-linear equation of motion to quickly and straightforwardly establish the reaction characteristics of a system in the non-equilibrium realm, providing access to detailed information about the reaction process, which would otherwise not be available. In addition, the evolution of key system properties provides a clearer physical picture of non-equilibrium behaviour and leads to a deeper understanding of the role played by the 2nd law of thermodynamics in the dissipative process.

A final point is that the computational burden involved in these calculations is minimal when compared to comparable methods in the literature. To date, model predictions have been made on a PC workstation and complete in a matter of seconds to a few hours depending on the complexity of the chemical reaction pathways that are considered. For those produced for this paper, the computational times are at the lower end. For a multi-phase, multi-component, nano-scale system with heat conduction, external applied field, diffusion, and multiple coupled electrochemical reaction pathways, the computational times are at the upper end. This is a huge advantage compared to the computational cost required by, for example, scattering calculations. Furthermore, since the solution is obtained via solving a set of first order ordinary differential equations, the memory requirement for solving the system models formulated using this framework is minimal, which contrasts with methods that depend on 3D grids of configurational space where the dimensionality grows exponentially. For this reason and the others demonstrated above, the SEA-QT framework has a great potential to contribute to the field of reaction kinetics for all phases of matter.

Acknowledgements

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