3D Quantum thermodynamic description of the non-equilibrium behavior of an unbounded system at an atomistic level

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Abstract. Quantum thermodynamics (QT) provides a general framework for the description of non-equilibrium phenomena at any level, particularly the atomistic one. This theory and its dynamical postulate are used here to model the storage of hydrogen on and in a carbon nanotube. The tube is placed at the center of a tank with a volume of 250 nm³. The thermodynamic system of interest is the hydrogen, which is assumed isolated and having boundaries that coincide with the walls of the tank and the carbon nanotube. The hydrogen is initially prepared in a state far from stable equilibrium (i.e., with the hydrogen molecules probabilistically near one of the outer tank walls) after which the system is allowed to relax (evolve) to a state of stable equilibrium. To predict this evolution in state, the so-called energy eigenvalue problem, which entails a many-body problem that for dilute and moderately dense gases can be modeled using virial expansion theory, is first solved for the geometry involved. The energy eigenvalues and eigenstates of the system found are then used by the nonlinear Beretta equation of motion of QT to determine the evolution of the thermodynamic state of the system as well as the 3D spatial distributions of the hydrogen molecules in time. The simulation results provide a quantification of the entropy generated due to irreversibilities at an atomistic level and show in detail the trajectory of the thermodynamic state of the system as the hydrogen molecules, which are initially arranged to be far from the carbon nanotube, spread out in the system and eventually become probabilistically more concentrated near the carbon atoms, which make up the nanotube.

1. Introduction
To develop a complete non-equilibrium description at a nano-scale, quantum thermodynamics (QT) can be used since it extends the linear dynamics of quantum mechanics (QM) to the non-linear dynamics required to describe systems undergoing a non-equilibrium process [1-17]. Note that QT is a paradigm distinct from and at variance to statistical (not conventional) quantum mechanics (SQM). From SQM, a whole set of Markovian and non-Markovian quantum master equations (QMEs) for so-called “dissipative open systems” have been developed. Applications of these QMEs have been somewhat limited (e.g., to optics, quantum electronic devices, Brownian motion of single particles, absorption and emission spectra, and molecular wires [18-23]). Furthermore, the dissipative description of these “open systems” relies on a closed-system-plus-reservoir model for which the time
evolution of state is governed by the standard Schrödinger and von Neumann equations. However, the underlying linear dynamics of these two equations is at variance with the dissipative (non-linear) nature of the QMEs derived from these equations (e.g., the well-known Kossakowski-Sudarshan-Gorini-Lindblad (KSGL) equation [24-27] or its equivalents). Irreversible relaxation to stable equilibrium is, thus, accomplished at the expense of introducing a paradox, i.e., the so-called Loschmidt paradox. In fact, common to all attempts at justifying the validity of these relaxations via QMEs is that they require additional, question-begging assumptions that are at odds with an overall unitary (i.e., reversible/linear) evolution [2]. In addition, although it is true that under appropriate conditions the response formalism of the QMEs can in certain cases be connected with the Onsager theory of irreversible processes [19], the perturbative theories governing these QMEs limit (as they do in the Onsager theory) their applicability to the near-equilibrium regime.

In contrast, QT and its equation of motion, the Beretta equation [2-11], circumvent these difficulties since the dissipations of the closed system minus the reservoir are assumed to be strictly endogenous to the system (contrary to the assumption made in SQM) and are fully captured by the nonlinear dynamics of the Beretta equation. QT, thus, is able to determine the non-equilibrium path, which the system takes and which once known, allows one to determine, for example, the non-equilibrium thermodynamic properties (e.g., the chemical potentials and affinities) of each species, the kinetics of any reactions present, and the entropy generated due to irreversibilities at each instance of time. The latter, in fact, represents the dissipation or destruction of the non-conserved system property, the available energy [28]. Furthermore, the path found is unique and fixed in an absolute sense at least to the extent that the relaxation times of QT are tied directly to experimental values and the time-energy Heisenberg uncertainty principle [16].

In this paper, QT is used to extend the work reported in previous papers [12-14] of modeling the non-equilibrium evolution in state of hydrogen storage on and in a carbon nanotube. The thermodynamic system of interest is the hydrogen, which is assumed isolated and contained within the walls of a 250 nm³ tank at the center of which lies the carbon nanotube. The system boundaries coincide with the walls of the tank and the tube. To model this evolution, the so-called energy eigenvalue problem, which entails a many-body problem that for dilute and moderately dense gases can be modeled using virial expansion theory [29,30], is first solved in 3D to determine the so-called primitive-level energy eigenvalues and eigenstates of the system. This information is then used in a combinatorial problem to determine the system-level energy eigenvalues and eigenstates. These are subsequently used in the nonlinear Beretta equation of motion of QT [2-11] to determine the evolution (relaxation) of the thermodynamic state of the system to stable equilibrium, starting from some initially prepared state far from stable equilibrium (i.e., with the hydrogen molecules probabilistically near one of the outer tank walls). The spatial distributions of the hydrogen molecules in time are then determined using the solutions found from the spatial and temporal parts of the QT description. The results of our simulations provide a quantification of the entropy generated due to irreversibilities at an atomistic level and show in detail the trajectory of the state of the system as the hydrogen molecules, which are initially arranged to be far from the carbon nanotube, spread out in the tank and eventually become more concentrated near the carbon atoms that make up the nanotube.

2. Application of QT

2.1. System description

The thermodynamic system under consideration is that of 4 H₂ molecules contained in a 5 nm x 5 nm x 10 nm tank with a carbon nanotube at its center. The nanotube is constructed based on [31] and is a (15,15) armchair carbon nanotube. The tube consists of a total of 900 atoms. The radius and the length of the tube are 1.017 nm and 3.56 nm, respectively. The carbon nanotube depicted in figure 1 is located at the center of the tank so that the center of the tube is placed at coordinates (5.0, 2.5, 2.5). The red spheres that comprise the tube represent the carbon atoms. The bonds connecting these atoms
are not represented. To simplify the model, it is assumed that the atoms and the structure of the nanotube remain stationary and do not vibrate.

2.2. Governing equations

Two systems of equations govern the evolution in time of the thermodynamic state and position of the H₂ molecules in the tank: one based on the Beretta equation of motion and the other on the energy eigenvalue problem. The former equation for a single constituent system is expressed in operator format by

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] - \frac{1}{\tau} \hat{D}$$

while the latter is written as

$$\hat{H}_i(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) = E_i u_i(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)$$

for $i = 1, 2, \ldots, L$. In Eq. (1), $\hat{H}$ is the Hamiltonian operator, $\tau$ a scalar time constant or functional, and $-\hat{D}/\tau$ the so-called dissipation term. The latter is a function of $\hat{\rho}$, $\ln \hat{\rho}$, and $\hat{H}$ and captures the nonlinear dynamics of an irreversible process by pulling the state operator or density matrix $\hat{\rho}$ in the direction of the projection of the gradient of the entropy functional $S = -k Tr(\hat{\rho} \ln \hat{\rho})$ onto the hyperplane of the constant energy (expectation value) of the system $E = Tr(\hat{\rho} \hat{H})$.

Eq. (1) implies both the first and the second laws of thermodynamics [1]. Furthermore, $\tau$ has a lower bound and, thus, $\hat{D}$ an upper bound based on the time-energy Heisenberg uncertainty relation [16]. In addition, the state operator $\hat{\rho}$ is a linear, self-adjoint, non-negative definite, unit-trace operator (i.e., an operator whose diagonal elements sum to one) on Hilbert space $\mathcal{H}$. At a given instance of time, it is a representation of the state of a system which catalogues how the energy of the system is distributed amongst the various system energy eigenlevels. This state operator is based on a homogeneous ensemble of identical systems, identically prepared, i.e., on an unambiguous preparation [15], which contrasts with the state operator of SQM that is based on a heterogeneous ensemble of identical systems, not identically prepared, i.e., on an ambiguous preparation. The former leads to an unambiguous unification of thermodynamics and mechanics with a single kinematics and a single dynamics.

As to the system of Eqs. (2), $E_i$ and $u_i$ are the system-level energy eigenvalues and eigenfunctions, the $\vec{x}_k$ are the 3D particle position vectors, and $L$ is the number of system-level energy eigenvalues. For the energies considered in this paper, only translational and rotational modes of energy storage
and their degeneracies are relevant and, thus, included in the quantum mechanical description. These modes of storage are modelled and solved separately here: the translational as a set of two-body problems solved numerically using a finite element approach and the rotational analytically. The resulting expression for the energy eigenvalues and degeneracies for the latter are presented in the next section. For translational modes, the Hamiltonian operator is given by

\[ \hat{H} = \sum_{k=1}^{n} \left( -\frac{\hbar^2}{2m} \nabla_k^2 + V_k(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n) \right) \]

and represents the kinetic and potential energies of the translational motions of the H\textsubscript{2} particles in the tank and the intermolecular interactions between H\textsubscript{2} particles and between the H\textsubscript{2} and C particles of the carbon nanotube.

2.2.1. The energy eigenvalue problem for rotation
Analytically, the rotational mode of energy storage for each H\textsubscript{2} molecule is modelled in its simplest form by assuming a rigid rotor model. The resulting eigenfunctions for the two degrees of rotational freedom are a product of an azimuthal quantum number \( m \) dependent exponential \[32\] and an angular momentum quantum number \( l \) dependent Legendre polynomial \[32\] such that \[29\]

\[ u_{l,m}(\theta, \phi) = \left[ \frac{(2l+1)[l-m]!}{2[l+m]!} \right]^{1/2} P_l^m(\cos \theta) e^{im\phi} \sqrt{2\pi}. \]

The corresponding rotational energy eigenvalue is expressed as \[29\]

\[ \epsilon_l = \frac{\hbar^2}{2I} (l + 1), \quad l \geq |m|, \quad m = 0, \pm 1, \pm 2, \ldots \]

where \( I \) is the moment of inertia equal to \( m_{rm} r^2 \), \( r \) the distance separating the hydrogen nuclei, and \( m_{rm} \) the reduced mass defined as

\[ m_{rm} = \frac{m_1 m_2}{m_1 + m_2}. \]

To account for the degeneracies of the number of rotational orientations as well as of the spin that leads to ortho- and para-hydrogen, the following expressions are used for the rotational and the ground state spin degeneracies \[29\]:

\[ g_l = 2l + 1 \]

\[ g_{sym}^{(1,2)} = g_0 (g_0 + 1)/2 \]

\[ g_{anti-sym}^{(1,2)} = g_0 (g_0 - 1)/2 \]

where \( g_0 \) is the ground-state spin degeneracy of a single nuclei equal to \( 2n+1 \) and \( n \) is the quantum spin number, which for the ground state is 1/2. Eq. (8) represents the symmetric spin degeneracy which leads to ortho-hydrogen and Eq. (9) the anti-symmetric spin degeneracy which results in para-hydrogen.

2.2.2. The energy eigenvalue problem for translation
The computational difficulties of the eigenvalue problem, which represents a multi-body problem, quickly augment as the number of particles in the system increases. In fact, it may even become impossible to solve. To circumvent this, a set of 2-body problems \[33\], which define the motions and interactions between pairs of H\textsubscript{2} molecules (an H\textsubscript{2} and its nearest neighbour) and between each of these two H\textsubscript{2} molecules and the C atoms located on the nanotube, can be assumed. Such an approach has been used very successfully when using QT to derive stable equilibrium property relations such as, for example, the virial equation of state. For the H\textsubscript{2}-C motions and interactions, which are of interest here, the 2-body problem is written as
\[ \hat{H}_k u_j(\vec{x}_k) = \epsilon_{k,j} u_j(\vec{x}_k), \quad j = 1, 2, \ldots, M \]  
for \( k = 1, 2 \) (i.e., the 1\textsuperscript{st} and 2\textsuperscript{nd} \text{H}_2) and the translational Hamiltonian operator is given by

\[ \hat{H}_k = -\frac{\hbar^2}{2m} \nabla^2 + \sum \epsilon \to (\vec{x}_k) \]

where the summation includes all of the \text{H}_2-C interactions. The potential functions \( V_{ij}(\vec{x}_k) \) are expressed by 6-12 Lennard-Jones potentials, i.e.,

\[ V(\vec{x}_k) = 4\epsilon \left[ \left( \frac{\sigma}{r(\vec{x}_k)} \right)^{12} - \left( \frac{\sigma}{r(\vec{x}_k)} \right)^{6} \right] \]

where \( r \) is the distance between molecules/atoms. Values for the fitting parameters \( \epsilon \) and \( \sigma \) specific to a particular interaction are given in table 1.

### Table 1. Fitting parameters for the L-J potential.

| Interaction | \( \epsilon \) (J) | \( \sigma \) (nm) |
|-------------|-------------------|-----------------|
| \text{H}_2-\text{H}_2 | 5.24 \times 10^{-22} | 0.2915 |
| \text{H}_2-C | 4.502 \times 10^{-22} | 0.3137 |

In Eq. (10), each \( \epsilon_{k,j} \) is a paired particle or so-called primitive-level energy eigenvalue related to the system-level energy eigenvalues \( E_i \), by

\[ E_i = \sum_{j=1}^{M} \nu_{ij} \epsilon_{k,j} \]

where \( M \) is the total number of primitive energy eigenvalues utilized and \( \nu_{ij} \) (the so-called occupation coefficient [33]) is the number of paired \text{H}_2-\text{H}_2 molecules for a given primitive energy eigenlevel \( j \) that occupies a given system energy eigenlevel \( i \). If only a single pair of \text{H}_2 molecules were present in the tank (i.e., for \( N=1 \)), all the occupation coefficients would be one. For the case of a closed, non-reacting system and \( N \geq 2 \), the number of system energy eigenlevels \( L \) is given by

\[ L = (N + M - 1)! / (N! (M - 1)!) \]

In general, the number of primitive energy eigenlevels is infinite for the translational Hamiltonian operator since this operator is unbounded. However, because of the computational burden of an infinite number of levels, a finite number \( P \) is assumed and of this finite number only a subset \( M \) is actually used, an assumption which under certain conditions is justified as described below.

For the paired \text{H}_2-\text{H}_2 motions, the 2-body problem is written as

\[ \hat{H}_{1,2} u_j(\vec{x}_1, \vec{x}_2) = \epsilon_{1,2,j} u_j(\vec{x}_1, \vec{x}_2), \quad j = 1, \ldots, M \]

and the Hamiltonian as

\[ \hat{H}_{1,2} = \sum_{k=1}^{2} \frac{-\hbar^2}{2m} \nabla^2_k + V(\vec{x}_1, \vec{x}_2). \]

This problem can equivalently be decomposed into a reduced mass \( (rm) \) and a center of mass \( (cm) \) problem [34] such that

\[ \hat{H}_k u_j(\vec{x}_k) = \epsilon_{k,j} u_j(\vec{x}_k), \quad j = 1, 2, \ldots, M. \]

In Eq. (17), \( k = rm, cm \); and the Hamiltonian for both the reduced mass and center of mass problems is expressed by

\[ \hat{H}_k = \frac{-\hbar^2}{2m_k} \nabla^2_k + V(\vec{x}_k). \]
For the reduced mass problem, the potential function \( V(\tilde{x}_\mu) \) is given by the 6-12 Lennard-Jones potential (Eq. (12)), while for the center of mass, it is zero. Furthermore, the reduced mass is defined by Eq. (6) above, the center of mass by

\[
m_{cm} = m_1 + m_2
\]

and the coordinates for each problem by

\[
\tilde{x}_{cm} = \frac{m_1 \tilde{x}_1 + m_2 \tilde{x}_2}{m_1 + m_2},
\]

(21)

Once the solutions to the set of 2-body problems listed above have been determined, they are assembled into a set of primitive-level energy eigenfunctions given by

\[
u_p(\tilde{x}) = u_{ijk}(\tilde{x}_1, \tilde{x}_2, \tilde{x}_{rm}, \tilde{x}_{cm}) = u_i(\tilde{x}_1) u_j(\tilde{x}_2) u_k(\tilde{x}_{cm}) \quad i, j, k = 1, \ldots, M \quad p = 1, \ldots, M^3.
\]

(22)

\( M \) represents the number of energy eigenvalue problems solved for each two-body problem. Neither the energy eigenfunctions for the center of mass nor for rotation are included in Eq. (22) because the energy eigenvalues for the former are two orders of magnitude below those of the other two-body eigenvalues and, thus, contribute little to each overall primitive-level eigenvalue and because for the latter the spatial and not the rotational orientation (a localized effect) of each hydrogen molecule in the tank is of interest here. However, as seen in Eq. (23), the rotational energies are included in the overall primitive-level eigenvalues since they are indeed significant, i.e.,

\[
e_p = e_{ijkl} = e_{i1} + e_{2j} + e_{rmk} + e_{rot}\quad i, j, k = 1, \ldots, M \quad l = 1, \ldots, \mathcal{R} \quad p = 1, \ldots, \mathcal{P}.
\]

(23)

Here \( \mathcal{R} \) and \( \mathcal{P} \) are the total number of possible degenerate rotational and primitive-level energy eigenvalues, respectively, that could be utilized. As explained below, the set of \( \mathcal{P} \) primitive levels represents a much larger set than the set of \( M \) primitive levels actually utilized.

Now, when two or more \( \text{H}_2-\text{H}_2 \) pairs are present (i.e., when \( N \geq 2 \)), a set of system-level energy eigenfunctions and eigenvalues must be determined based on the primitive-level ones utilized (i.e., the set of \( M \) levels). This is done by first determining the \( v_{ip} \) coefficients in Eq. (24) via a combinatorial problem which fills an \( L \times M \) matrix of possible occupation energies from which the system-level energy eigenvalues, \( E_i \), are found using

\[
E_i = \sum_{p=1}^{M} v_{ip} e_p.
\]

(24)

To find the system-level \( u_i \), the primitive-level \( u_p \) are first projected from the decomposed space represented by \( (\tilde{x}_1, \tilde{x}_2, \tilde{x}_{rm}) \) back onto 3D space represented by \( (\tilde{x} = \{x, y, z\}) \) and then combined using

\[
u_i(\tilde{x}) = \prod_{p=1}^{M} (u_{ip}(\tilde{x}))^{v_{ip}}.
\]

(25)

This last result, Eq. (25), is a set of spatially dependent eigenfunctions, which are independent of time since the Hamiltonian operator and the boundary conditions (i.e., the tank walls and location of the carbon atoms) are fixed.

2.2.3. The equation of motion

To complete the thermodynamic description of the process, which the system of figure 1 undergoes, the solutions of the energy eigenvalue problem just described must be combined with those of the system of equations formed by the equation of motion, Eq. (1). In addition, since this is an initial-value problem, an initial condition for the system, i.e., an initial non-equilibrium state represented by an initial state operator or density matrix \( \hat{\rho} \), must be determined. This can be done randomly or by using the procedure outlined in [35], which finds a set of partially canonical equilibrium states and then perturbs them to find a set of initial non-equilibrium states. Another approach and the one used
here is to adjust the probabilities of the state matrix so that the likelihood of the hydrogen pairs at or near the boundary of the tank is very high.

Now, assuming that $\hat{\rho}$ is diagonal in the $\hat{H}$ representation, $\hat{H}$ and $\hat{\rho}$ commute and Eq. (1) reduces to

$$\frac{d\hat{\rho}}{dt} = -\frac{1}{\tau} \hat{D}. \quad (26)$$

Note that according to the Beretta equation, an initial $\hat{\rho}$, which is diagonal in the $\hat{H}$ representation, remains so at all times $t$. This special class of diagonal initial states is used here for simplicity and because in this case the eigenvalue $\rho_i$ of $\hat{\rho}$ is readily interpreted as the probability of finding the system in the system-level energy eigenvalue $E_i$. Nonetheless, it should be emphasized that the Beretta equation yields well-defined evolutions for arbitrary non-equilibrium initial states $\hat{\rho}$ not necessarily diagonal in the $\hat{H}$ representation, i.e., when $\hat{H}$ and $\hat{\rho}$ do not commute.

Eq. (21) written out in terms of the eigenvalues $\rho_i$ (probabilities) of $\hat{\rho}$ (for this particular case, the diagonal elements of $\hat{\rho}$) yields (for $i=1,...,L$)

$$\frac{d\rho_i}{dt} = -\frac{1}{\tau} \left[ \sum_{i} \rho_i \ln \rho_i \right] - \frac{1}{\tau} \left[ \sum_{i} E_i \rho_i \right] + \frac{1}{\tau} \left[ \sum_{i} E_i^2 \rho_i \right]. \quad (27)$$

The dissipation term in Eq. (26) or (27) moves the system’s entropy in the local direction of “steepest entropy ascent” [2] at constant energy $E = \sum_{i=1}^{L} \rho_i E_i$ and composition. This is expressed explicitly in terms of the time evolution of $S = -k \sum_{i=1}^{L} \rho_i \ln \rho_i$ by the entropy balance written as

$$\frac{dS}{dt} = k \frac{1}{\tau} \left[ \sum_{i} \rho_i \ln \rho_i \right] + \frac{1}{\tau} \left[ \sum_{i} E_i \rho_i \right] - \frac{1}{\tau} \left[ \sum_{i} E_i^2 \rho_i \right]. \quad (28)$$

where the entropy generation term to the right of the equals is always non-decreasing.

2.2.4. Evolution in time of the thermodynamic state and position

Finally, with all the eigenvalues $\rho_i$ of the state operator $\hat{\rho}$ known at each instance of time $t$ and the system-level eigenfunctions $u_i$ as a function of the spatial coordinates $\vec{x}$, the probability distribution function $\Phi(\vec{x},t)$ for the evolution in time and space of the state of the hydrogen particles in the tank is found from

$$\Phi(\vec{x},t) = \sum_{i=1}^{L} \rho_i(t) |u_i(\vec{x})|^2. \quad (29)$$

The first moment of this distribution function, used in the results presented below, is the mass density expressed as a function of time by

$$\rho(t) = \frac{\int \int \Phi m_{H_2} n dV}{\int \int dV} \quad (30)$$

where $m_{H_2}$ is the mass of a hydrogen molecule and $n$ the number of these molecules in the system.
3. Coarse graining the energy eigenlevels

3.1. Need for coarse graining
The complexity of solving the energy eigenvalue problem goes up markedly with the number of spatial dimensions considered (i.e., 1D, 2D, or 3D [12-14,35]). Consequently, for our 3D calculations, eigensolutions spanning only a limited energy range are calculated because our codes to date have only run on high-end PC workstations. Future work entails modifying and transporting the code to the massively parallel supercomputer, System X, available at Virginia Tech. For the results presented here, however, only two hundred eigensolutions \( (M=200) \) are calculated for each translational two-body problem. Despite this limited number, the total number of possible primitive levels turns out to be \( P=M^3R = 1.2 \times 10^8 \). If all of these are actually used so that \( M=P \), then for the case of \( N=2 \), the number of system levels \( L \) explodes to something on the order of \( 10^{15} \). Obviously, for computational reasons, this number must be reduced to something more manageable, and this is done via the technique of coarse graining the energy eigenlevels.

3.2. Coarse graining
A coarse graining scheme is used here in which bundles of many system energy eigenlevel occupation trajectories are replaced with single representative trajectories. This is an improvement over our previous work [12], which also used methods that amounted to coarse graining in order to limit the number of levels and, thus, trajectories. However, the coarse graining employed in the present work is done in a more systematic way with the underlying justifications being more carefully considered.

In the context of our work, trajectories are traces that describe how the occupation probabilities of the energy eigenlevels of our system vary over time. They depict as a function of time the probability that a given energy eigenlevel will be occupied by the system. Figure 2 illustrates how the trajectories for energy eigenlevels that lie within a restricted energy range, i.e., within a so-called “bundle”, tend to evolve similarly in time and might, therefore, be replaced by a single, judiciously chosen trajectory. The computational burden can thereby be reduced while retaining the major dynamical characteristics of the system.

Figure 2. Solution of the Beretta equation for a set of energy eigenlevels over a limited energy range, i.e., for a so-called “bundle” of trajectories with energies close to one another and behaving similarly in time.

In order to help validate our coarse graining technique, we compare the results of coarse graining to the exact solutions for a given sample system. This is possible as long as the number of trajectories is not too large. The maximum number of trajectories that we have been able to solve to date on a high-end PC workstation has been on the order of a million. The exact results for a system having this
many or fewer trajectories are, thus, compared to our coarse grained results. Provided the correlation between the coarse grained and the exact solution for this limiting case is good, a reasonable assumption is that the coarse grained results can be extrapolated to even higher numbers of levels for which exact solutions are not possible.

Figure 3 compares a set of trajectories from an exact solution with their coarse grained counterparts. In order to compare the fewer number of coarse grained trajectories with those for the exact solution, the number of trajectories for the latter is reduced by averaging their effects over the same energy ranges used to determine the bundles for the coarse grained trajectories. In figure 3, the averaged trajectories of the exact solution are steeper than those for the coarse grained solution, but the two sets of trajectories are seen to start at the same initial values and end at very near the same stable equilibrium values, thus, providing credence for the use of coarse graining as an approximate method. Of course, this leaves open the question of the proper scaling of the magnitude of the coarse grained solution since it necessarily underestimates that of the exact solution. This is addressed below.

As to determining the coarse graining itself, the technique used is to divide the entire energy range for the full number of energy eigenlevels into bundles having an equal number of levels. The level having the median index (quantum number) within a given bundle is chosen as representative of that bundle. The coarse grained levels, thus, reflect the overall density of levels for the larger system. Where the levels for the larger system are closely spaced or sparse, the coarse grained approximation is also closely spaced or sparse.

Figure 3. Coarse grained and exact trajectories are compared in a normal (figure on the left) and a magnified (figure on the right) view; paired trajectories (coarse and exact) have the same color with the steeper slope indicating the trajectory from the exact solution and the gentler the coarse grained one.

Now, the differences in trajectory slopes seen in figure 3 indicate that coarse graining introduces errors in magnitude that must be addressed if this technique is to be used to model larger systems. The number of trajectories affects, for example, the magnitude of the entropy of the system as well as the speed at which the system evolves towards stable equilibrium. Since the entropy for a given system energy is proportional to the natural log of the number of energy eigenlevels available to the system, the entropy of the coarse grained system will necessarily be lower than that for the larger (i.e., exact) system. In addition, systems accessing a higher density of energy eigenlevels also evolve more quickly. Thus, these effects must be taken into account by properly scaling the coarse grained results. If the scaling of the entropy and the time evolution of the coarse grained system is correctly done, the overall changes in entropy and the occupation probabilities with time can be made to closely represent the behavior of the larger system.
Figure 4 illustrates how coarse grained results are scaled to represent those of the larger system. In this figure, 20 energy eigenlevels representing the coarse grained system are used to represent a system with 10,000 levels as illustrated by this diagram of entropy versus time. Proper scaling of the amplitude of the coarse grained curve allows one to match the full range of entropy for the larger system. Furthermore, by compressing the time axis, the slope of the trace is steepened and the rate of time evolution is made to correspond to the large system. Finally, a time shift is required to place the approximate curve on top of the curve for the larger system. Slight deviations are seen between the actual curve and the approximate one, but with these three simple scaling procedures a surprisingly close correspondence is achieved.

Figure 4. Scaling example of how a small number of coarse grained energy eigenlevels can closely approximate the collective behavior of many levels if proper scaling is used.

Figures 5 to 10 below provide relationships for the scaling factors for entropy, the time scale, and the time shift associated with the system depicted in figure 1. Two sets of scaling factors are needed: one for the primitive energy eigenlevels representing one hydrogen pair followed by the other for the system energy eigenlevels representing two hydrogen pairs. It is apparent from the primitive level data in figures 5 to 7 that all three of scaling factors are proportional to the log of the

Figure 5. Entropy scale factor as a function of primitive levels; the scaling factor is based on 200 coarse grained levels.

Figure 6. Inverse of the time scale factor as a function of primitive levels; the scaling is based on 200 coarse grained levels.
primitive energy levels \( M \) that are utilized in the simulation. In contrast, the system-level scaling for two hydrogen pairs as shown in figures 8 to 10 is based on the expression

\[
L = M(M + 1)/2. \tag{31}
\]

Since the number of system levels goes up geometrically instead of exponentially, the system-level scaling factors approach asymptotic values as \( M \) gets large.

4. Numerical approach

4.1. Numerical approach for solving the energy eigenvalue problems for translation

Each of the two-body eigenvalue problems for translation is numerically solved by the finite-element method (FEM). A proper weak formulation is used to apply FEM to this problem, namely,

\[
\int \nabla \Phi \cdot V u \, d\Omega + \int \Phi L u \, d\Omega = \epsilon \int \Phi u \, d\Omega \tag{32}
\]

where \( \Phi \) is the test function and \( \epsilon \) the eigenvalue considered. The solution \( U \) is approximated by second order Lagrange polynomials \( \Phi_j \), i.e.,
From Eqs. (32) and (33), the following generalized eigenvalue problem is deduced:

\[ K\tilde{u} = \beta M\tilde{u} \]  

(34)

where \( K \) is the stiffness matrix, and \( M \) is the mass matrix, the elements of which are given by

\[ K_{ij} = \int \nabla \varphi_i \cdot \nabla \varphi_j d\vec{x} + \int V(\vec{x}) \varphi_i \varphi_j d\vec{x} \]

(35)

\[ M_{ij} = \int \varphi_i \varphi_j d\vec{x} \]

(36)

For the case of the center of mass (cm) problem, the potential is zero in which case the stiffness matrix becomes

\[ K_{cm,ij} = \int \nabla \varphi_i \cdot \nabla \varphi_j d\vec{x} \]

(37)

Matrices \( K \) and \( M \) are properly modified to match the boundary conditions. The generalized eigenvalue problem is then solved by the Arnoldi algorithm \([36, 37]\) applied to a shifted and inverted matrix with restarts until the eigenvalues are found. Solutions are considered converged after the residuals are less than \( 1.0 \times 10^{-6} \). The adopted grid consists of an unstructured mesh of 149,000 elements to ensure a grid independent solution.

4.2. Numerical approach for solving the Beretta equation of motion

A system of 20,100 first order ordinary differential equations (ODEs) are generated from the Beretta equation of motion and used to determine the evolution in state of the system in figure 1. This system of equations is solved numerically forward and backwards in time using a Runge-Kutta 4,5 (RKF45) method, starting from an arbitrarily chosen dimensionless time of \( t^* = -2 \). This Runge–Kutta–Fehlberg method \([38–40]\) uses a fourth order approach together with a fifth order one by employing all of the points of the former plus one additional calculation required by a Runge-Kutta 5 method. The RKF45 method is, thus, able to estimate and control the error in the solution and determine an appropriate step size automatically. This makes the method efficient for ordinary problems of automated numerical integration of ODEs.

5. Results and discussion

Figures 11 to 14 show the evolution in time of the probability distribution function (Eq. (29)) for the
system of figure 1 comprised of four hydrogen molecules ($N=2$) and the 900 carbon atoms that make up the carbon nanotube. At the initial (non-equilibrium) state at $t^*= -2.0$ (-9.5 unscaled), one can see in figure 11 that the highest values of the probability distribution function and, therefore, the highest densities (the dark red) of hydrogen occur in and around the tube as well as away from the tube and towards the bottom wall of the tank. In figure 12, this picture has evolved so that in this new non-equilibrium state at $t^*= -0.224$ (-2.0 unscaled), one can see a somewhat greater concentration of hydrogen inside the tube and nearer the outside tube walls. The concentration of hydrogen near the bottom of the tank has also increased as has the hydrogen in the upper part of the tank.

From this last state, the state of the system evolves to the state shown in figure 13. This new intermediate non-equilibrium state occurs at $t^*= 0.4894$ (1.0 unscaled). As can be seen in this figure, the state of the system has evolved to the point that the value of the probability distribution function and, thus, the density of hydrogen has significantly decreased at the bottom of the tank and concentrated even more in and around the carbon nanotube.
Figure 13. Plot of the probability density (probability distribution function) of particle position as a function of position at an intermediate non-equilibrium state at $t^* = 0.4894$ (1.0 unscaled) with $N=2$, $M=200$, and 20,100 system energy eigenlevels utilized.

Finally, figure 14 shows the final state of the system in stable equilibrium at $t^* = 1.198$ (4.0 unscaled). As should be evident from the figure, the highest values of the probability distribution function and, thus, the hydrogen densities (the dark red) occur in the tube and close to the outer walls of the carbon nanotube. However, the hydrogen density inside the tube has decreased somewhat to $5.6 \times 10^{-5}$ kg/m$^3$ from its previous value of $6.1 \times 10^{-5}$ kg/m$^3$ at $t^* = 0.4894$ (1.0 unscaled). This can be seen more clearly in figure 15, which shows the evolution of the hydrogen mass density as a function of time. Furthermore, the greater densities observed here in the interior of the tube are consistent with what has been observed both in a limited number of experiments and in, for example, the molecular dynamic (MD) simulations published in the literature [41]. Note also that the temperature at stable equilibrium is about 27.9 K which means that the hydrogen quantum molecular model used here is consistent with a gaseous state for the hydrogen since hydrogen has a triple point temperature of 14 K at 0.07 atm.

Figure 14. Plot of the probability density (probability distribution function) of particle position as a function of position at stable equilibrium at $t^* = 1.198$ (4.0 unscaled) with $N=2$, $M=200$, and 20,100 system energy eigenlevels utilized.
Figure 15. Plot of the mass density of hydrogen stored inside the carbon nanotube as a function of time.

Now, in order to assess the irreversibilities which occur during the thermodynamic process depicted in the previous figures, one can examine the rate of entropy generation as well as the change in the entropy due to irreversibilities. Both are shown in figure 16 and both results are scaled to represent the larger system with its $10^{15}$ system energy eigenlevels. The vast majority of the entropy creation and, thus, the increase in the entropy of the system occurs in a time interval of $\tau^*=0.3$ to $\tau^*=0.6$. This corresponds with the largest number of energy eigenlevels coming into play, taking up a share of the overall system's energy and becoming occupied as the state of the system moves towards the stable equilibrium (canonical) distribution (see figure 17). Note that the gaps in the energy eigenlevels seen in figure 17 are due to our current inability to calculate enough translational eigenvalues ($M=200$ currently) to fully span the energy range up to the lowest rotational energy eigenlevel.

Figure 16. Evolution in time of the entropy generation rate (figure on the left) and the entropy (figure on the right); both have been scaled to represent the results of the larger system with $10^{15}$ system energy eigenlevels.

In order to view the evolution in state of the system in figure 1 in another more traditional light, the probability density distribution of energies is calculated for the non-equilibrium states through which the system passes as well as for the stable equilibrium state at which the system arrives. The
results for the latter state and for two of the three non-equilibrium states are shown in figure 18. As can be seen, there is an evolution from a non-Maxwellian type of distribution at $t^*= -2.0$ and at $t^*=0.224$ to a Maxwellian type of distribution at stable equilibrium. This is what one would expect but what is significant here is that one does not have to guess at the distributions since they fall directly out of the physics/thermodynamics of the problem captured by both the Beretta equation of motion and the energy eigenvalue problem associated with the behavior of the hydrogen molecules relative to each other and to the carbon atoms in the tank. As in figure 17, the gaps in the distribution occur due to our current inability to calculate enough translational eigenvalues ($M=200$ currently) to fully span the energy range up to the lowest rotational energy eigenlevel.

Finally, to determine the minimum number of finite energy eigenlevels required for modeling the evolution of state of the system to an acceptable level of accuracy, a plot of the system energy $E$ (an expectation value) versus the system entropy $S$ (also an expectation value) is made for different numbers of eigenlevels including the so-called limit curve of an infinite number of levels. The results are shown in figure 19 along with the maximum thermodynamic temperature at which the accuracy for a given number of finite energy eigenlevels begins to decrease. As can be seen, with 20,100 coarse grained system energy eigenlevels utilized, the system can be modeled with good results for temperatures at stable equilibrium up to about 27.9 K. After that, the stable equilibrium curve for 20,100 levels begins to diverge significantly from the limit curve which is based on an infinite number of levels. To achieve higher temperatures, more system energy eigenlevels would have to be used. It
should also be emphasized here that the thermodynamic temperature only has meaning at stable equilibrium and is not defined for non-equilibrium states. This, however, unlike in other approaches (e.g., MD), poses no problem for describing the thermodynamic evolution of state of the system since the equation of motion, the Beretta equation, does not require it.

Figure 18. Expectation energy $E$ versus the expectation entropy $S$ for the hydrogen in the 3D tank with $N=2$ and $M=200$ and the number of coarse grained system energy eigenlevels varying between 100 and 20,000.

6. Conclusions

QT has been applied successfully here to modeling the 3D thermodynamic evolution in state and position of an atomistic or nanoscale system of hydrogen molecules contained in a tank at the center of which is a carbon nanotube. The thermodynamic description in time which results provides the exact path taken by the system in relaxing from some initial state far from stable equilibrium to a final state of stable equilibrium. The current improvement of our model to three dimensions holds the real prospect of being able to make future comparisons to the results of other well accepted simulation methods as well as experimental data. Such comparisons cannot help but be useful in making improvements to the present QT hydrogen storage model as well testing QT predictions with real world results.

Finally, the successful application of this new paradigm has been limited to date since any number of issues or problems remain to be resolved including how this paradigm can be applied to a much wider range of practical problems of interest (reacting systems, open systems, systems undergoing non-work interactions, high temperature systems, etc.). We are presently working on many of these issues.

Appendix

$\hat{D}$ dissipation operator
$E$ expectation energy
$E_i$ system-level energy eigenvalue
$\hat{H}$ Hamiltonian operator
$\hbar$ Planck’s constant divided by $2\pi$
$k$ Boltzmann’s constant
$L$ number of system energy eigenlevels
$M$ number of system energy eigenlevels
$m$ mass
$N$ number of primitives
\( n \) number of particles or molecules
\( S \) expectation entropy
\( t \) time
\( t^* \) dimensionless time equal to \( t/\tau \)
\( u(\vec{x}) \) energy eigenfunction
\( V(\vec{x}) \) interparticle potential function
\( \vec{x} \) coordinate vector
\( x \) \( x \)-coordinate
\( y \) \( y \)-coordinate
\( z \) \( z \)-coordinate

Greek:
\( \epsilon \) fitting parameter for the L-J potential
\( \epsilon_p \) primitive-level energy eigenvalue
\( \Phi(\vec{x}, t) \) probability distribution function of particle position in time
\( \nu \) occupation coefficients
\( \rho \) state operator or density matrix
\( \sigma \) fitting parameter for the L-J potential
\( \tau \) scalar time constant or functional

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