Molecular Dynamics by Quantum Mechanics

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Abstract
Traditional MD simulations of chemical reactions with temperatures given by the equipartition theorem are problematic as atom temperatures are forbidden by the Planck law of quantum mechanics. MD proceeds without temperature with thermal effects simulated with the momentum of heat flow from IR lasers. MD simulations of RIXS experiments proceeds by specifying X-ray momentum.

1.0 Introduction
Traditionally, MD simulations of chemical reactions are thought [1] mediated through changes in the positions of the reactant atoms induced by temperature induced molecular vibrations based on the equipartition theorem. MD stands for molecular dynamics. MD assumes the temperature T of the atoms is given by the average kinetic energy <KE> of atoms in an ensemble by the equipartition theorem of statistical mechanics,

$$T = 2 < KE >/3N \tag{1}$$

where, <KE> is the average kinetic energy of the atoms and N the number of atoms in the ensemble. MD simulates changes in atom positions in a continuum of chemical reactants by applying PBC to an ensemble of a small number of atoms in a computational box. PBC stands for periodic boundary conditions. Although the equipartition theorem and PBC are traditional in MD, there are questions as to the validity of the MD simulations.

One question is whether atoms in a continuum under PBC do indeed simulate the chemical reactions. The finite size of computation box [2] is likely to introduce interaction between molecules in the continuum of periodic images, especially if long range electrostatic forces are simulated. Moreover, the equipartition theorem is violated [3] in MD simulations with PBC if fluctuations are not allowed for the center of mass of the computation box. Regardless, chemical reactions occur locally between atoms of reactant molecules having nothing to do with the average temperature of atoms in the ensemble representative of the continuum. A more fundamental question is whether MD based PBC and the equipartition theorem can be extended to discrete molecules.

In applying MD to discrete molecules, PBCs are problematic. Indeed, the MD simulations of protein folding are commonly performed with PBC, even though folding is a discrete process unrelated to the continuum. Moreover, application of the equipartition theorem of classical physics to discrete molecules is precluded by the Planck law of QM that requires atoms have vanishing heat capacity, i.e., positional changes of atoms in discrete molecules therefore have nothing to do with temperature. QM stands for quantum mechanics. Figure 1 shows the Planck law at ambient 300 K temperature giving the heat capacity of the atom in terms of the wavelength λ of EM confinement.
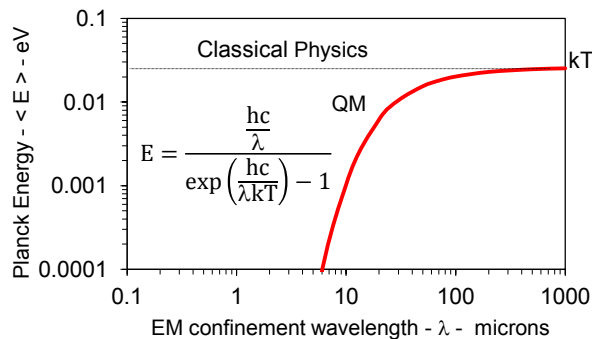
Figure 1. Planck law of QM at 300 K

Classical physics is depicted by a horizontal line allowing the atom to always have kT energy from the macroscale > 1000 microns to the nanoscale < 1 micron. QM differs by requiring the kT energy of the atom to decrease below 100 microns and vanish at the nanoscale < 1 micron. Hence, heat cannot be conserved in a molecule < 1 micron by an increase in temperature, thereby precluding the notion of relating the velocity of atoms in discrete molecules to their temperature. However, the equipartition theorem is valid in MD simulations of the continuum >100 microns under PBC as atoms have kT energy and do indeed change in temperature.

2.0 Problem

MD aside, the fact discrete molecules are precluded by QM from increasing in temperature while the equipartition theorem is not applicable to single molecules suggests molecules cannot vibrate, a false conclusion refuted by observation. Indeed, chemical reactions obviously do occur as atoms change position by molecular vibration. So the question is:

Why do molecules vibrate?

Indeed, the same question may be asked why MD finds basis in the equipartition theorem. There is no question temperature is somehow connected to molecular vibration, but a physical mechanism is required which cannot be the esoteric equipartition theorem.

3.0 Background

In RIXS, an external source of X-rays [4] positions the atoms in a molecule. But what about ordinary chemical reactions absent X-rays? Since QM precludes temperature changes, whether the heat Q from an ambient thermal bath can accumulate for electronic energy in core electrons to reach the K-edge level was considered [5] and found to take < 100 ps. But X-ray absorption in RIXS typically occurs in < 100 fs. Since a 1000 fold reduction in absorption times is unlikely, ordinary chemical reactions cannot be initiated by X-rays created from an ambient thermal bath,

What is the mechanism inducing the molecular vibrations
that positions atoms and yet be consistent with QM?

4.0 Purpose
The purpose of this paper is to present MD simulations of heat Q from IR lasers to show how traditional programs may be modified consistent with QM for discrete molecules without invoking the equipartition theorem. The nitrogen molecule in the stretch mode is used to show how directional heat flow Q from IR lasers can control ordinary chemical reactions

5.0 Mechanism
A molecular vibration is excited when the molecule absorbs a photon with a quantum $n = 1$ of energy $E = h\upsilon$. When two quanta are absorbed the first overtone is excited, and so on to higher overtones. A transition from level n to level $n+1$ due to absorption of a photon, the frequency of the photon is equal to the classical vibration frequency. For the H·Cl molecule, the overtones may even lead to dissociation at D_o as illustrated in Figure 2.
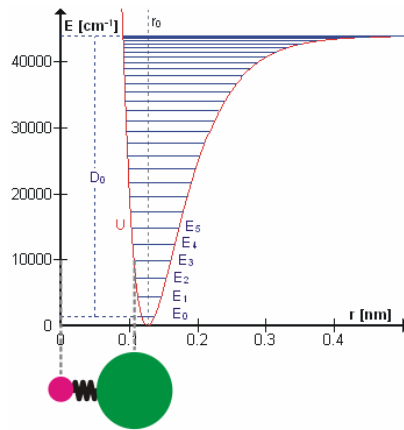

Figure 2. Vibration levels of the H·Cl molecule

However, excitation of molecule by photons differs with heat flow rate Q from a thermal bath. Photons must have precise frequencies to match the overtone levels, but atom temperatures from classical physics are continuous and not discrete. Because of the nanoscopic size of molecules, QM by the Planck law forbids the classical heat transfer as temperatures cannot change. Hence, the molecule directly converts heat flow Q into n quanta of $E = h\upsilon$ in the ground state,

$$Q\Delta t \; = n \, h\upsilon \tag{2}$$

where, Δt is the time of heat Q absorption, but must be sufficiently spontaneous. Following RIXS, say $\Delta t < 100$ fs.

Over time Δt, the heat flow Q under the EM confinement of the vibrational ground state $h\upsilon$, that for nitrogen is in the IR. Overtones are not excited. Under the same EM confinement frequency υ of the vibrational ground state, the heat flow Q creates n identical IR photons, each having energy $E = h\upsilon$ exciting molecular vibration in the IR.

Similar QM arguments have been made [6] for the creation of UV, VIS, and IR photons from absorbed heat Q in nanostructures. Like vibration, the photons are created because QM forbids the conservation of heat Q by temperature. Instead, the high surface-to-volume ratio of nanostructures places interior atoms under high EM confinement as the heat Q is concentrated in their surfaces allowing photons to stand across the nanostructure. Once the photons are created, the EM confinement vanishes and the photons are absorbed by the material of the nanostructure or escape to the surroundings. The frequency υ of photons created is, $\upsilon = c/\lambda$, where λ is the wavelength of the standing photon, $\lambda = 2\,n_r\,d$, and n_r is the refractive index of the nanostructure.

6.0 Analysis

Similarly, MD by QM initiates chemical reactions by molecular vibration from the conversion of directional heat flow Q to the mode of the nitrogen molecule. The heat Q provided by a IR laser having frequency υ matched to the vibration frequency of the nitrogen molecule,

$$Q \sim n\left(\frac{hc}{\lambda}\right) / \left(\frac{\lambda}{c}\right) = \frac{Pc^2}{\lambda}\ J/s \tag{3}$$

where, P is the photon momentum, $P = n\,h/\lambda$, and n is the number of IR photons confined to the stretch quantum state. Heat flow Q directed along the bond direction of the nitrogen molecule to excite the stretch mode having frequency υ is shown in Figure 3.

IR Laser Heat
$Q \sim J/s$

Nitrogen

Molecular Vibration
$E = n\,h\upsilon$

Figure 3. Momentum of Heat Flow

However, the heat flow Q is restricted by the time τ to reach the quantum $E = h\upsilon$ by $\tau = n\,h\upsilon/Q$. Over time Δt, the momentum P is constant and force $F = P/\Delta t$. In the MD solution, the initial velocity V of the atom mass m is imposed in the first iteration, $V = F\Delta t/m = P/m$.

7.0 Simulation

Standard MD programs are modified for QM by updating the impulse force F at each iteration depending on the direction of momentum P, but temperature fluctuations are excluded consistent with QM. The implementation is simple as the directionality of momentum forces $\Delta F = P/\Delta t$ between a pair of atoms is already implicit in the L-J computation of forces, say in the leapfrog algorithm [1] prior to computing atom velocities. L-J stands for Lennard-Jones. Figure 4 depicts a 2D (x, y) model of a molecule driven by forces F from momentum P of an IR or X-ray source.
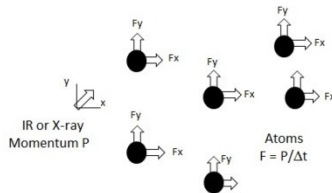

Figure 4 2D Model for Impulse Forces

The MD of the nitrogen molecule in the stretch mode is simulated with a half-model by fixing the central anti-node of the molecule shown in Figure 5.
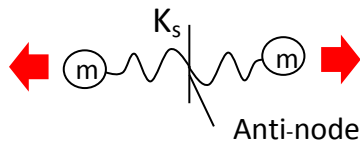

Figure 5 Model of Nitrogen Molecule

The nitrogen stretch mode is modelled by a bead-spring force $F = K_s(x - d/2)$, where d is the bond length. Spring stiffness K_s is selected to simulate experimental nitrogen resonance in the IR at 2330 /cm ~ $7x10^{13}$ Hz.

The MD solutions for the nitrogen molecule in the stretch mode for the heat flux Q of 320 mW comprising 10^5 IR photons having frequency $\upsilon = 7x10^{13}$ Hz matched to the stretch mode of the nitrogen molecule. The integration time step $\Delta t = 1 \times 10^{-17}$ s. The MD response for the amplitude X and velocity V of the nitrogen atom are shown in Figure 5.
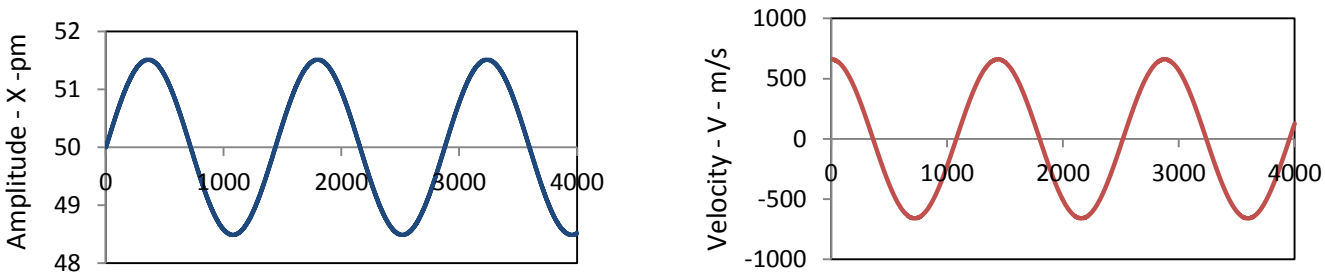

Figure 5 Amplitude and velocity of the Nitrogen atom
under 320 mW IR laser excitation at $7x10^{13}$ Hz

In the first iteration, the Q = 320 mW IR laser supplies the nitrogen atom with n = 10^5 IR photons in time $\tau = n\ h\upsilon/Q = 14.5$ fs. What this means is the nitrogen molecule stretch mode is filled with photons as Bosons in time $\tau < 100$ fs that is sufficiently spontaneous to justify the superposition of quantum states. Moreover, the momentum P provided by 10^5 IR photons is actually 2 orders greater than that from a single 434 eV ray photon having wavelength $\lambda = 2.86$ nm. But unlike IR lasers, synchrotron X-ray radiation is not always available for the common chemical reaction.

Regardless, a continuously variable IR laser capable of being tuned to the frequency of stretch and bending vibration modes of typical molecules is required, but is not available. However, if developed may lead to IR control of chemical reactions. In this regard, study is now underway.

8. Conclusions

The path toward a theory for MD by QM holds the promise of improving the IR or X-ray control of chemical reactions. This paper has taken a step in that path by demonstrating agreement between atomistic MD simulations of the stretch mode of molecular nitrogen. A summary of the findings is as follows.

MD by QM supersedes traditional MD simulations of RIXS experiments under synchrotron radiation by avoiding the erroneous temperature changes in X-ray heating predicted by the equipartition theorem of classical physics.

Ordinary chemical reactions absent X-rays may be initiated by the QM induced conversion of directional heat flux Q from common strip heaters in thermal baths. But heat Q from continuously variable IR lasers is preferred as the IR frequency can be tuned to the specific stretch or bending modes of reactant molecules as in RIXS with X-rays. Indeed, the momentum $P = n\,h/\lambda$ from only $n \sim 10^3$ IR photons is comparable to a single X-ray photon having wavelength $\lambda = 3$ nm. Hence, IR lasers and not X-rays from synchrotrons are suggested for the practical control of chemical reactions.

In MD simulations of X-rays in controlled synchrotron experiments, implementation of QM by the Planck law is straightforward because the traditional leapfrog algorithm that updates the L-J forces every iteration depending on the directionality between a pair of atoms may readily include the impulse forces from IR or X-ray sources.

Heat flow Q from the momentum of IR or X-ray lasers for the nitrogen stretch mode is not significant to change bond lengths because of the high stiffness suggesting the bending modes having greater flexibility in combination with L-J forces actually mediate chemical reactions.

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