Molecular Dynamics by X-rays?

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Abstract

MD simulations of chemical reactions mediated by the vibrational positions of atoms in reactant molecules show the equipartition theorem defining atom positions by their kinetic energy depending on temperature is problematic as the atom temperatures are forbidden by the Planck law of quantum mechanics. Instead, atoms are positioned by the momentum of X-rays emitted from other atoms. The stretch mode of the nitrogen molecule is used to show how modifications in traditional MD programs may be made for X-ray control of chemical reactions.

1.0 Introduction

Traditionally, chemical reactions are thought mediated through changes in the positions of the reactant atoms induced by temperature induced molecular vibrations. Indeed, 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. MD stands for molecular dynamics and PBC for periodic boundary conditions. MD assumes [1] the temperature T of the atoms is given by the average kinetic energy <KE> of atoms in the ensemble by the equipartition theorem of statistical mechanics,

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

where, N is the number of atoms in the ensemble. Although the equipartition theorem and PBC are invariably used 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 molecules and do not depend on an average temperature of atoms in the computation box. But if so, 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, one might consider atom temperatures related to the average kinetic energy of each molecule. Indeed, the MD simulations of the folding of proteins is commonly performed with PBC, even though folding is a discrete process unrelated to the continuum. Fundamentally, the 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. QM stands for quantum mechanics. Positional changes of atoms in discrete molecules therefore have nothing to do with temperature. Figure 1 shows the Planck law at ambient temperature giving the heat capacity of the atom in terms of the wavelength λ of EM confinement.
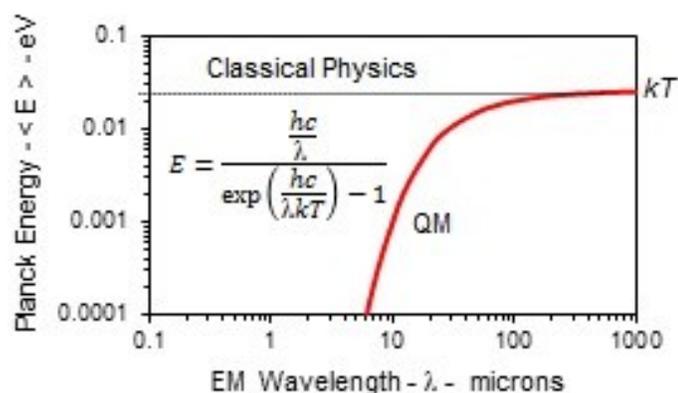
Figure 1. Planck law of QM

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 by an increase in temperature, thereby precluding the notion of relating the velocity of atoms in discrete molecules to their temperature. Conversely, atoms in MD simulations of molecules in a continuum under PBC are correctly assumed have kT energy and allowed to change in temperature consistent with the equipartition theorem.

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 by temperature, a conclusion refuted by observation. Indeed, chemical reactions do occur as atoms change position by molecular vibration. So the question is:

How 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 and cannot be the equipartition theorem.

3.0 Proposal
Chemical reactions occur by atoms conserving heat by emitting X-rays that excite the vibrational modes of the reactant molecules. Temperature is not involved as QM precludes conservation of heat into temperature. Instead, heat is conserved by increasing core electrons above the ground state, the process continuing until, say the K-edge level is reached, at which time the atom emits the corresponding X-rays. The X-rays move radially outward to excite vibration modes of the reactant molecules. The depleted core electron energy of the atoms are regained by heat flow into the atom from the surroundings, the process forever repeated.

4.0 Background
The notion of MD by X-rays evolved from a review of recent RIXS experiments [4] that showed specific vibrational modes of a molecule could be excited by external X-rays, although vibrational mediated chemistry has been known [5,6] for over a few decades. RIXS stands for resonant inelastic X-ray scattering spectroscopy. Excitation of molecular vibration in a ground electronic state with light from a laser was shown [5] to become the reaction coordinate for dissociation allowing the approach of a reactive atom, if in the direction of the reaction coordinate, to initiate a bimolecular reaction. Similarly, a particular reaction pathway in single NH3 was selected [6] by adjusting the electronic tunneling current and energy during the reaction to activate either the stretching vibration of ammonia or the inversion of its pyramidal structure. In RIXS, externally supplied X-rays are tuned to the symmetric stretching of a molecule while other tunings may excite bending modes.

However, RIXS has a more fundamental importance. Given the equipartition theorem in relating atom velocities to average temperatures is questionable and ordinary chemical reactions absent RIXS occur without external X-rays suggests that atoms may somehow be emitting their own X-rays. But if so, the long-standing paradigm that chemical reactions are initiated by changes in positions of atoms in molecules depending on their temperature may need to be revised to one based on positional changes by X-rays. Provided a mechanism is found that converts heat in atoms to X-rays instead of temperature, the equipartition theorem in MD that defines atomic vibrations from atom temperatures may no longer be needed in the simulation of chemical reactions.

5.0 Purpose
The purpose of this paper is to present a procedure for MD simulations by X-rays. But given the enormity of this undertaking, only a simple nitrogen molecule in the stretch mode is considered, other more complex molecules are studied later.

6.0 Mechanism
Lacking heat capacity by QM, thermal heat cannot increase core electron temperature with conservation proceeding by increasing the electron energy E. Treating the electron [7] as a continuous ring of radius R, the energy E,

$$E = hc/n\lambda = hc/2\pi R \qquad (2)$$

The standing electron waves consist of n wavelengths λ around the circumference of a ring or radius R, where $n\lambda = 2\pi R$, n = 1,2,3,... For an atom in the human body at 40 C, the heat flow Q into the electron is estimated from that into a spherical cavity of ring radius R in a water bath at ambient temperature T = 310 K,

$$Q = 4\pi R^2(\Theta T/R) = 4\pi\Theta RT \qquad (3)$$

where, Θ is the thermal conductivity, $\Theta = 0.61$ W/m-K and T = 310 K. The time τ to fill the K-edge is, $\tau = E/Q$. The X-ray energy E and time τ to fill the depleted K-edge core electron n = 1 level in terms of the electron radius R is shown in Figure 2.
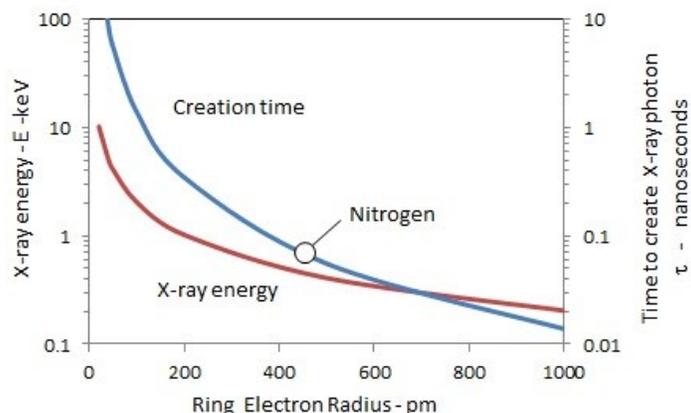
Figure 2. X-ray energy and core electron filling time

The K-edge absorption for the nitrogen atom having electron energy $E = 0.434$ keV corresponds to an electron ring radius $R = 469$ pm. Hence, $Q = 1.11 \times 10^{-6}$ J/s $= 62$ ps. The X-ray emission then excites other atoms by fluorescence including 50 meV phonons and charge transfer > 2 eV as depicted in Figure 3.
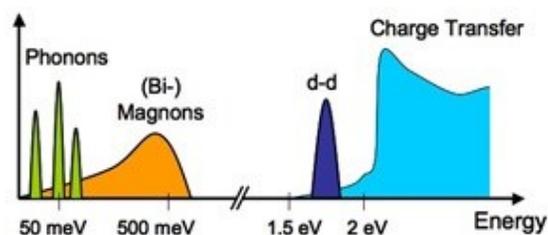

Figure 3. X-ray induced fluorescence

7.0 Simulations

Standard MD programs are modified for QM by updating atom momentum P at each iteration depending on the direction of X-rays emitted and absorbed from all atoms, but temperature fluctuations are excluded consistent with QM. Figure 4 depicts a 2D (x, y) model of a molecule driven by X-rays at the instant the central atom releases K-edge energy.
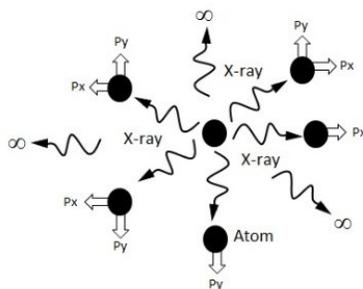

Figure 4 2D Model for X-ray Interaction

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 4a.
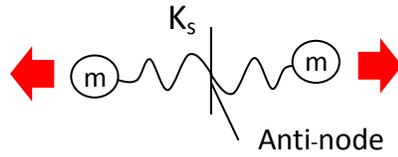
Figure 4a Model of Nitrogen Molecule

The nitrogen stretch is modeled by a bead-spring, $F = K_s(x - d/2)$, where d is the bond length. Spring stiffness K_s is selected to simulate experimental resonance, 2331 /cm ~ 7×10^{13} Hz

7.1 MD of Nitrogen by X-rays
7.1.1 Inelastic Energy
Depending on the inelastic energy Eo absorbed, the X-ray from one atom in the nitrogen pair imparts an initial velocity V to the other atom along the longitudinal direction,

$$V = \sqrt{2Eo/m} \tag{4}$$

where m is the mass of the nitrogen atom and Eo $= \eta E$, $\eta \ll 1$. For inelastic X-ray energy Eo = 10 meV, the initial velocity V = 371 m/s. The MD solution by inelastic energy was obtained at temperature of 310 K for 20,000 iterations at time step $\Delta t = 10^{-16}$ s and agrees with theory as shown in Figure 5.
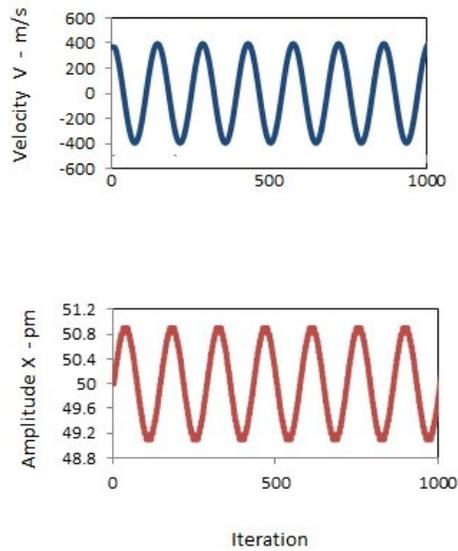

Figure 5 MD by Inelastic Energy

To provide a comparison with QM, the MD solution by the equipartition theorem was also derived for the nitrogen molecule in the stretch mode. The temperature was held at 310 K by scaling the velocities [1] every iteration by a factor,

$$\text{Factor} = \sqrt{F/T} \tag{5}$$

where, F = desired temperature. The current temperature T from (1) by the equipartition theorem,

$$T = 2k <KE>/3 \rightarrow Vnew = Vold * Factor \qquad (6)$$

Velocity scaling is used in thermal equilibration of MD models in slow transients. But for fast transients like nitogen in the stretch mode, Figure 6 shows the equipartition theorem results differ significantly from the MD by Inelastic Energy solution in Figure 5.
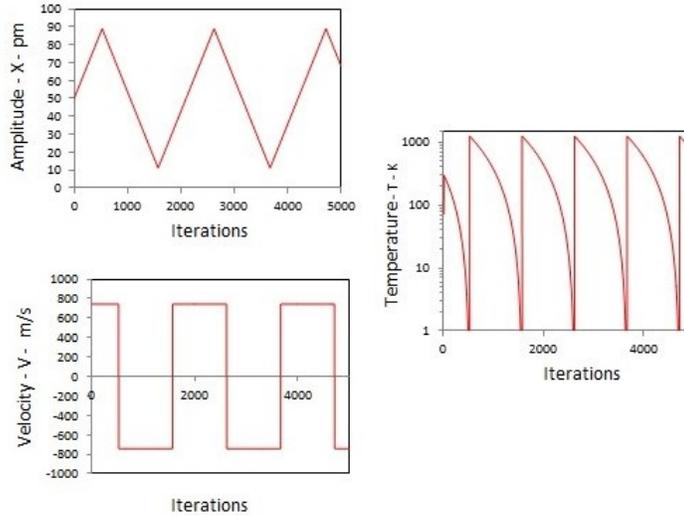

Figure 6. MD by Equipartition Theorem

7.1.2 Momentum

In MD by X-ray momentum, the force F applied each time step Δt is, $F = P / \Delta t$. For a time step $\Delta t = 10^{-16}$ s, nitrogen, $F = 2.35 \times 10^{-11}$ Nt. The acceleration $\alpha = F/m = 1.0 \times 10^{17}$ m/s^2. Over the time step, the nitrogen atom velocity and displacement are, $V = \alpha \Delta t = 10$ m/s and $x = \alpha t^2 /2 = 0.0005$ pm. Since the nitrogen molecule has a stretch frequency $f = 2261/cm = 6.78 \times 10^{13}$ Hz, the period $\tau = 0.0147$ pm. Hence, the MD solution may be resolved with about 30 points/cycle as shown in Figure 7.
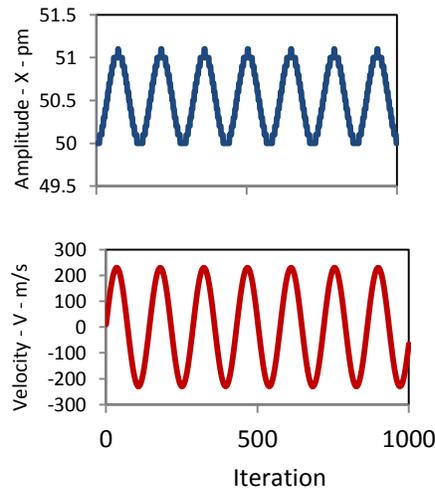

Figure 7. MD by Momentum

8. Harmonic Response Analysis

RIXS response [2] showing vibrational excitation (0.2 eV) superposed on the core electron (434 eV) was confirmed with a harmonic response analysis for a 2 DOF model of the nitrogen atom and core electron shown in Figure 8.
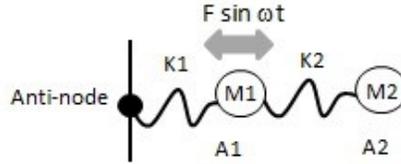

Figure 8. 2 DOF Atom-Electron Model

The mass of the atom M1 and electron M2 are suspended on respective stretch springs K1 and K2. The atom is driven by a harmonic force $F \sin \omega t$ with response amplitudes A1 and A2. The nitrogen atom properties were K1 = 2*2261 Nt/m, M1 = 14/Avag, and M1 = 2.32×10^{-26} kg. The electron mass M2 = 9.31×10^{-31} kg. The core electron energy E2 = 434 eV coresponds to frequency f2 = E2/h = 1.05×10^{17} Hz and stretch stffness K2 = M2$(2\pi f2)2$ = 395000 Nt/m. The amplitudes A1 and A2 are:

$$A1 = \frac{P1(K1 + K2 - M2\omega^2)}{(K1 + K2 - M1\omega^2)(K2 - M2\omega^2) - K2^2} \tag{7}$$

$$A2 = \frac{P1K2}{(K1 + K2 - M1\omega^2)(K2 - M2\omega^2) - K2^2}$$

Figure 8 shows the core electron is excited by nitrogen vibrations, but the magnitude is small. But for P1 = 1 Nt , the nitrogen atom amplitude A1 = 0.04 m gives an electron amplitude A2 = 4×10^{-9} m, therefore A2 / A1 = 1×10^{-7} is small, but finite.
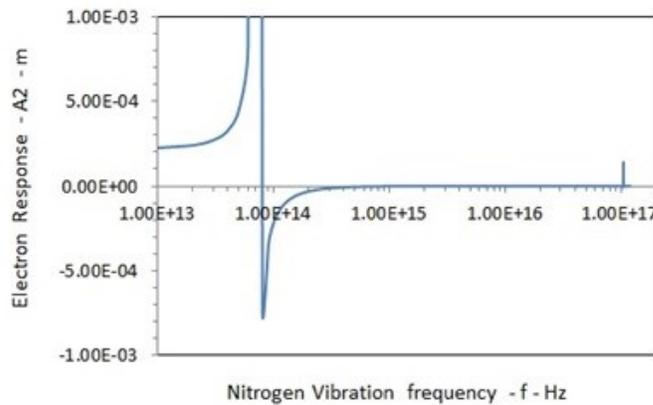

Figure 8. Electron 2 DOF frequency response to Nitrogen excitation

9. Conclusions

The path toward a theory for MD by X-rays holds the promise of improving the understanding of chemical reactions. This paper has taken a step in that path by demonstrating agreement between atomistic MD simulations and experimental X-ray results. A summary of the findings are as follows.

9.1 PBC

MD simulations of the continuum by PBC that assumes the atoms have heat capacity is consistent with QM and is unequivocally valid. However, whether the MD simulations have any meaning is unlikely as discreteness most likely controls the positions of atoms and local chemical reactions. Specifically, the numerous MD simulations of protein folding in the literature by PBC, although consistent with statistical mechanic, have little physical meaning.

9.2 Equipartition Theorem

MD simulations have invariably assumed the equipartition theorem as the way of calculating the positions of atoms in reactant molecules. Indeed, statistical mechanics gives the positions of atoms from the average kinetic energy <KE> of a PBC ensemble to be related to the temperature T of the PBC ensemble, $<KE> = 3 kT/2$. Although valid for chemical reactions the continuum, statistical mechanics is not valid for chemical interactions between discrete molecules .

9.3 X-rays

QM controls the chemical reaction between atoms in discrete molecules. Core electrons are treated as a finite ring allowing a QM treatment as a physical particle instead of a point. Like atoms by the Planck law, the core electrons therefore have vanishing heat capacity and upon heating cannot increase in temperature. Because heat cannot increase the core electron temperature, conservation proceeds by increasing core electron energy levels to the K-edge of the atom, at which time an X-ray photon is emitted. The short filling time < 60 ps allows the core electron transition to K-edge levels to occur spontaneously.

MD simulations of nitrogen molecule based on the X-ray momentum $P = h/\lambda$ at the 434 eV K-edge show the stretch mode vibrations are correctly excited at 2261 cm^{-1}. The force F applied to the nitrogen atom each iteration Δt was $F = P/\Delta t$ while the QM requirement of no temperature changes was maintained. In contrast, the equipartition MD solution gave unrealistic atom temperatures. Instead of applying the momentum force F, imposing initial velocities $\Delta V = P/m$ was found more difficult to implement. In the leapfrog MD algorithm, the X-ray forces are conveniently accumulated along with the spring (or LJ) forces before updating current velocities.

9.4 Harmonic Response

RIXS showed molecular vibration (0.2 eV) superposed on K-edge response (434 eV). To understand how RIXS could measure small vibrations at K-edge levels, a harmonic response spectrum for a 2 DOF simulation of the core electron attached to the nitrogen atom showed that a small, but finite response of the core electron to atom excitation does indeed occur.

References

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