

Energy equipartitioning in the classical time-dependent Hartree approximation

John E. Straub^{a)} and Martin Karplus

Department of Chemistry, Harvard University Cambridge, Massachusetts 02138

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In the classical time-dependent Hartree approximation (TDH), the dynamics of a single molecule is approximated by that of a "field" (each field being N "copies" of the molecule which are transparent to one another while interacting with the system via a scaled force). It is shown that when some molecules are represented by a field of copies, while other molecules are represented normally, the average kinetic energy of the system increases linearly with the number of copies and diverges in the limit of large N . Nevertheless, the TDH method with appropriate energy scaling can serve as a useful means of enhancing the configurational sampling for problems involving coupled systems with disparate numbers of degrees of freedom.

Many systems of interest are composed of more than one type of molecule. To calculate time-averaged properties, molecular dynamics or Monte Carlo simulation can be used. If one is interested in the gas phase scattering of two molecules X and A , many trajectories are calculated and averaged over the simulated scattering events. For a condensed phase system composed of many molecules of type A (the solvent), and only a few of type X (the solute), most of the computation is spent on the molecules of type A , while the information desired often concerns averages for molecules of type X . To simplify the problem, the time-dependent Hartree approximation (TDH)^{1,2} can be introduced. In this approximation, molecules of one type are assumed to move in the mean field of molecules of other types. For example, the dynamics of a particular molecule can be approximated by a "field" of N "copies" of the molecule. Each copy sees the full force of a normal molecule while each normal molecule sees only $1/N$ th of the force from each copy. This approach has proved to be useful in the study of vibrational energy transfer in the scattering of small molecules,¹ where an equal number of copies N is used for all molecules of the system. (For two types of molecules there are N^2 possible interactions of all copies of the first molecule with all copies of the second molecule.) A corresponding method has been applied recently to the study of ligand diffusion in the protein myoglobin where only the ligand is represented by multiple copies.² Since the protein makes up most of the atoms in the system, such a simulation is much less costly than N separate ligand protein simulations. From one simulation of a single protein and N ligand copies in the TDH representation, statistical information about the distribution of N ligand-protein systems was obtained. In both applications, the TDH approximation led to enhanced sampling of averaged properties.

In this note, we consider the question of the equipartitioning of energy in the TDH approximation. In Newtonian dynamics, energy is equipartitioned and each degree of freedom has an average kinetic energy equal to one-half the thermal energy. We show that in the TDH approximation, when one molecule is represented by a field of copies, while other

molecules are represented normally, the average kinetic energy of each copy increases linearly with the number of copies and diverges in the limit $N \rightarrow \infty$.

In classical mechanics, molecules move according to Newton's equations of motion. For simplicity, we consider a system composed of molecules of type A and type X . The kinetic energy is

$$K = \frac{1}{2} \sum_A M_A \sum_{k=1}^3 \dot{q}_{Ak}^2 + \frac{1}{2} \sum_X M_X \sum_{k=1}^3 \dot{q}_{Xk}^2, \quad (1)$$

where the subscript $k = 1, 2,$ and 3 represents the Cartesian coordinates $x, y,$ and z . The potential energy can be written

$$V = V_{AA}(q_A) + V_{AX}(q_A, q_X) + V_{XX}(q_X), \quad (2)$$

where M_A is the mass and q_A and \dot{q}_A are positions and velocities for molecules of type A ; the same holds for molecules of type X . $V_{AA}(q_A)$ contains the potential energy of interaction between molecules of type A and the internal potential of type A molecules; $V_{XX}(q_X)$ is defined correspondingly for molecules of type X . $V_{AX}(q_A, q_X)$ is the potential energy for molecules of type A interacting with molecules of type X .

For such an isolated Newtonian system, the total energy ($E = K + V$) is conserved in time. There are $3N_A$ equations of motion

$$M_A \ddot{q}_{Ak} = - \frac{\partial V_{AA}(q_A)}{\partial q_{Ak}} - \frac{\partial V_{AX}(q_A, q_X)}{\partial q_{Ak}} \quad (3)$$

for the N_A atoms composing molecules of type A , and $3N_X$ equations of motion

$$M_X \ddot{q}_{Xk} = - \frac{\partial V_{AX}(q_A, q_X)}{\partial q_{Xk}} - \frac{\partial V_{XX}(q_X)}{\partial q_{Xk}} \quad (4)$$

for the N_X atoms composing molecules of type X .

For a canonical or microcanonical ensemble of constant (average) energy, there will be an allowable phase space, or energy surface. We assume that the system is ergodic so that any trajectory will, given enough time, explore the entire energy shell. Further, we define the canonical ensemble average as

$$\langle \dots \rangle = \frac{\int d\Gamma \dots e^{-H(\Gamma)/k_B T}}{\int d\Gamma e^{-H(\Gamma)/k_B T}}, \quad (5)$$

where the integral $\int d\Gamma$ forms an average over the phase

^{a)} National Institutes of Health Postdoctoral Fellow. Present address: Department of Chemistry, Boston University, Boston, MA 02215.

space Γ , $H(\Gamma)$ is the Hamiltonian, k_B is the Boltzmann constant, and T is the temperature. For such a system, the kinetic energy obeys the equipartition theorem. The canonical ensemble average kinetic energy for each degree of freedom in the system is equal to $1/2 k_B T$. Thus, the average kinetic energy of each degree of freedom k of each atom composing a molecule of type A is

$$\langle \frac{1}{2} M_A \dot{q}_{Ak}^2 \rangle = \frac{k_B T}{2} \quad (6)$$

and for type X

$$\langle \frac{1}{2} M_X \dot{q}_{Xk}^2 \rangle = \frac{k_B T}{2}. \quad (7)$$

For the TDH system, composed of molecules of type A (treated normally) and N copies of each molecule of type X , the kinetic energy is assumed to have the renormalized form

$$K = \frac{1}{2} \sum_A M_A \sum_{k=1}^3 \dot{q}_{Ak}^2 + \frac{1}{2N} \sum_X M_X \sum_{i=1}^N \sum_{k=1}^3 \dot{q}_{Xik}^2 \quad (8)$$

and the potential energy is taken to be

$$V = V_{AA}(q_A) + \frac{1}{N} \sum_{i=1}^N [V_{AX}(q_A, q_{Xi}) + V_{XX}(q_{Xi})]. \quad (9)$$

If we define the Lagrangian $L = K - V$, the equations of motion for the TDH system follow from Lagrange's equation; that is

$$M_A \ddot{q}_{Ak} = - \frac{\partial V_{AA}(q_A)}{\partial q_{Ak}} - \frac{1}{N} \sum_{i=1}^N \frac{\partial V_{AX}(q_A, q_{Xi})}{\partial q_{Ak}} \quad (10)$$

for atoms composing molecules of type A , and

$$M_X \ddot{q}_{Xik} = - \frac{\partial V_{AX}(q_A, q_{Xi})}{\partial q_{Xik}} - \frac{\partial V_{XX}(q_{Xi})}{\partial q_{Xik}} \quad (11)$$

for atoms composing the i th copy of molecule X . The total energy $E = K + V$, with K and V defined by Eqs. (8) and (9), is conserved. The conjugate momentum for coordinate q_{Ak} is defined

$$p_{Ak} = \frac{\partial L}{\partial \dot{q}_{Ak}} = M_A \dot{q}_{Ak} \quad (12)$$

as expected. However, for coordinate q_{Xik} the conjugate momentum is

$$p_{Xik} = \frac{\partial L}{\partial \dot{q}_{Xik}} = \frac{M_X}{N} \dot{q}_{Xik} \neq M_X \dot{q}_{Xik}. \quad (13)$$

This is a statement that the system is non-Newtonian because all interactions do not involve equal and opposite forces.

An approach to obtaining the kinetic energy distribution is to map the TDH equations of motion into an isomorphic Newtonian system. Making the following substitutions:

$$\begin{aligned} \frac{M_X}{N} &\rightarrow m_X, \\ \frac{V_{AX}(q_A, q_{Xi})}{N} &\rightarrow v_{AX}(q_A, q_{Xi}), \\ \frac{V_{XX}(q_{Xi})}{N} &\rightarrow v_{XX}(q_{Xi}), \end{aligned} \quad (14)$$

in Eqs. (8) and (9) we have the kinetic energy

$$K = \frac{1}{2} \sum_A M_A \sum_{k=1}^3 \dot{q}_{Ak}^2 + \frac{1}{2} \sum_X m_X \sum_{i=1}^N \sum_{k=1}^3 \dot{q}_{Xik}^2 \quad (15)$$

and the potential energy

$$V = V_{AA}(q_A) + \sum_{i=1}^N [v_{AX}(q_A, q_{Xi}) + v_{XX}(q_{Xi})]; \quad (16)$$

Eqs. (8) and (9) form a Newtonian system. The equations of motion follow from Hamilton's equations:

$$M_A \ddot{q}_{Ak} = - \frac{\partial V_{AA}(q_A)}{\partial q_{Ak}} - \sum_{i=1}^N \frac{\partial v_{AX}(q_A, q_{Xi})}{\partial q_{Ak}} \quad (17)$$

for molecules of type A , and

$$m_X \ddot{q}_{Xik} = - \frac{\partial v_{AX}(q_A, q_{Xi})}{\partial q_{Xik}} - \frac{\partial v_{XX}(q_{Xi})}{\partial q_{Xik}} \quad (18)$$

for the i th copy of molecule X . Equations (17) and (18) are equivalent to Eqs. (10) and (11) in that the trajectory generated for the positions q_{Ak} and q_{Xik} is the same. The average kinetic energy of each degree of freedom of each atom composing a molecule of type A is

$$\langle \frac{1}{2} M_A \dot{q}_{Ak}^2 \rangle = \frac{k_B T}{2} \quad (19)$$

and for type X

$$\langle \frac{1}{2} m_X \dot{q}_{Xik}^2 \rangle = \frac{k_B T}{2}. \quad (20)$$

Thus, if the kinetic energy per copy is defined as in Eq. (8), equipartition is satisfied. However, since there are N copies, the total kinetic energy per degree of freedom for the N copies equals $Nk_B T/2$. Inverting the mapping of Eqs. (14) to obtain the original system, it follows that for each degree of freedom of each copy of molecule X with normal mass M_X the kinetic energy would be

$$\langle \frac{1}{2} M_X \dot{q}_{Xik}^2 \rangle = \frac{Nk_B T}{2} \quad (21)$$

and that the average kinetic energy of the TDH system with $3N_A$ degrees of freedom for the atoms composing molecules of type A and N copies of each of the N_X atoms composing molecules of type X is

$$\langle K \rangle = (N_A + N \cdot N_X) \frac{3k_B T}{2}. \quad (22)$$

The average thermal kinetic energy per degree of freedom of molecule X increases linearly as the number of copies. This is a direct result of the non-Newtonian character of the equations of motion. Equation (22) should be used as the definition of the temperature in terms of the kinetic energy defined by Eq. (8). When one simulates a microcanonical ensemble with the TDH method it is important to recognize that as N increases the total energy would have to be increased to produce a desired average temperature [Eq. (22)]. For example, assume one performs a microcanonical average of the Newtonian system according to Eqs. (3) and (4) and calculates the average kinetic and potential energies associated with a particular total energy E for the system. If the corresponding system is simulated in the TDH approximation according to Eqs. (10) and (11) with the same total energy

E , the kinetic energy will be concentrated in the copies of the X variables and the total system temperature corresponding to Eqs. (8) and (22) will be less than desired. To achieve the desired temperature T , the energy of the TDH system would have to be increased to E_{TDH} , according to

$$E_{\text{TDH}} = \langle V_{\text{TDH}} \rangle + \left(\frac{1 + N \frac{N_X}{N_A}}{1 + \frac{N_X}{N_A}} \right) [E - \langle V \rangle], \quad (23)$$

where E and $\langle V \rangle$ are the total and average potential energies of the Newtonian system, and E_{TDH} and $\langle V_{\text{TDH}} \rangle$ are the total and average potential energies of the TDH system. However, without a knowledge of $\langle V_{\text{TDH}} \rangle$ it is not possible to determine in advance the energy E_{TDH} necessary to achieve the desired average temperature. If the system were harmonic, E_{TDH} would be

$$E_{\text{TDH}} = E \left(\frac{1 + N \frac{N_X}{N_A}}{1 + \frac{N_X}{N_A}} \right). \quad (24)$$

For enhanced sampling and the calculation of averaged properties, the simpler procedure to achieve a desired average temperature in a microcanonical ensemble is to rescale the velocities of the copies of type X so that the average mean-square kinetic energy per atom *per copy* is $3 kT/2$. Note that if all molecules in the system are represented by an equal number of copies, energy equipartition is satisfied. That is the case in the application of TDH to small molecule scattering by Gerber *et al.*¹

If there are internal degrees of freedom for the molecules of type X , the average internal potential energy for each molecule X_i [contained in $V_{XX}(q_{X_i})$] will reflect the increased average kinetic energy. If each molecule X_i is a harmonic oscillator, the virial theorem will be satisfied and the

average potential energy for each oscillator will be $N kT/2$, reflecting the increase in kinetic energy. Also, since the mean-square velocity of each copy increases as N the time scale for the motion of the degrees of freedom of X_i will be shorter than for the A degrees of freedom. For large N , if no velocity rescaling is done it may be necessary to use a multiple time-step algorithm to efficiently integrate the equations of motion.

Finally, we note that the divergence in the mean square velocity ($\langle \dot{q}_{X_{ik}}^2 \rangle$) in the TDH system can be avoided by using the idea of an isomorphic classical system. Scaling the mass of each copy of particle X by a factor of N to $\hat{M}_X = NM_X$ results in an average mean square velocity of

$$\langle \dot{q}_{X_{ik}}^2 \rangle = \frac{NkT}{\hat{M}_X} = \frac{kT}{M_X} \quad (25)$$

which is what is desired for ensemble averaging in the mean field approximation. This substitution replaces a divergence in the thermal energy of the copies with a divergence in the mass. However, if we are interested in configurational averages, a scaling in the mass will not alter the results. Alternatively, the TDH method with appropriate energy scaling can serve as a useful means of enhancing the configurational sampling for problems involving coupled systems with disparate numbers of degrees of freedom.

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