Molecular Dynamics Simulations of Chemical Reactions for Use in Education

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The computational power of computers available to students has increased to the point that it is now feasible to build interactive molecular simulations that can be used in education. In this paper, the simulation engine of an open source program called the Molecular Workbench *(1)*, which can simulate thermodynamics of chemical reactions, is described. While calculating the time evolution of the system, the software also generates rich, dynamic visual representations of the system that help students understand the salient features of a dynamic system. The user can easily start, stop, and examine frame-by-frame any specific simulation and can quickly change the starting conditions and parameters. This type of real-time, interactive simulation and visualization of chemical reactions at the atomic scale could help students understand the connections between chemical reaction equations and atomic interactions. Observing chemical reactions as emergent behaviors from the time evolution of an atomic-scale model is expected to help learners build intuitive, coherent, and predictive mental models of chemical reactions *(2, 3)*.

Molecular dynamics in education

Educators have been interested in molecular dynamics (MD) software since microcomputers were first available. Early efforts used a hard-sphere model that could reproduce ideal gas behavior remarkably well *(4-6)*. More recently, the programming language *NetLogo* has been used to give students the ability to create their own models of ideal gases *(7)*. These models cannot simulate liquids or solids because they lack attractive forces among atoms, although they could be easily added to *NetLogo*. To simulate any condensed state, and most phase transitions, attractive forces between atoms are needed. Less educational programs based on attractive forces have been developed, probably because the computers available to students have only recently had the computational power required. Two sources of software that show phase transitions are available to educators; one is the *Virtual Molecular Dynamics Laboratory (8)* and the other from a commercial company *(9)*.

This paper reports the addition of chemical reactions to a classical MD modeling system for educational use. Compared with research-grade simulations using sophisticated *ab initio* MD methods *(10)*, which are usually vectorized and run on high-end machines, our main goal is to build a working model accessible to the majority of chemistry teachers for teaching the thermodynamics of chemical reactions. Therefore, the requirements about real-time visualization and interactivity are far more important than they are for software intended for research. Not only must the software compute the motion of an ensemble of atoms, it must also generate a rich set of visual representations of the system on a real-time basis while remaining responsive to users' inputs. Bearing these needs in our mind, we chose to use simple rules for reactions in conjunction with classical MD to build a model capable of generating chemical reaction kinetics satisfactory for classroom use. The resulting model runs reasonably quickly on current personal computers. Through its graphical user interface (GUI), the software can illustrate in a visual and interactive manner important thermodynamic concepts, such as elementary reactions, reaction rates, chemical equilibrium, exothermic and endothermic reactions, and catalysis.

Adding reaction mechanisms to molecular mechanics

According to molecular mechanics *(11)*, in 2D, a molecule is a group of atoms interconnected by elastic bonds defined by radial and angular spring forces. These bonds are usually not breakable in a conventional implementation of molecular mechanics. In order to simulate reactions that are essentially processes of reorganizing molecules, however, rules for forming and breaking bonds have to be introduced. Once such rules are established, the reaction simulation is simple: use classical MD to compute the time evolution of the system, and then at regular intervals, search every atom for conditions that might lead to an elementary reaction. In each case that has sufficient energy to make new bonds and/or break the involved bonds, the software makes the changes and then continues the MD computations. The changes, usually in the interatomic forces and velocities of the interacting atoms, can thus be propagated spatially and temporally, and ultimately contribute to the thermodynamics of the entire system.

It is assumed that the static electronic energy associated with the formation of molecules (i.e. when the bond lengths and angles are in the equilibrium positions of their vibrations) can be expanded in the following localized form[1]:

$$U_{\text{Elec.}} = \sum_{m \in \text{bonds}} \mu_m^l + \sum_{n \in \text{angles}} \mu_n^g$$

where μ_m^l is the part of the electronic energy associated with the bond m when the distance between the bonded pair equals the equilibrium bond length, and μ_n^g is that associated with an adjacent pair of bonds that make an angle n when the angle equals the equilibrium bending angle. The parameters μ_m^l and μ_n^g are critically important to the reaction energetics, and will be referred to as *chemical energies* throughout this paper, in order to avoid confusion with other energies. The interatomic forces are derived from the following potentials acting on each atom:

$$U = V_{\text{VDW}} + V_{\text{EL}} + V_{\text{BS}} + V_{\text{AB}}$$

with

$$V_{\text{VDW}} = \frac{1}{2} \sum_{i,j,i \neq j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}} \right)^6 \right]$$

$$V_{\text{EL}} = \frac{1}{2} \sum_{i,j,i \neq j} \frac{q_i q_j}{R_{ij}}$$

$$V_{\text{BS}} = \frac{1}{2} \sum_{m \in \text{bonds}} k_m^l (l_m - l_m^0)^2$$

$$V_{\text{AB}} = \frac{1}{2} \sum_{n \in \text{angles}} k_n^\theta (\theta_n - \theta_n^0)^2$$

where V_{VDW} is the van der Waals energy, V_{EL} the electrostatic potential energy, V_{BS} the bond-stretching energy, and V_{AB} the angle-bending energy. The item-by-item explanation of the mathematical symbols are omitted here to save space. Interested readers can consult Ref. 11. The motion of each atom is calculated using classical equations of motion according to the forces derived from these potentials using standard methods *(11)*.

Chemical reactions: a simple system

There is nothing in the previous equations that accounts for changing bonds. Additional rules are needed to model chemical reactions involving bond formation and breaking.

Reaction pathways: n-body elementary reactions

The program periodically examines every current bond to determine whether there is sufficient energy to break it, and every possible pair of sufficiently close free radicals to see whether a bond should be made between them. The decisions are made on the basis of energy-conserving rules. This approach is well suited for simple elementary reactions. Thus, a reaction consisting of several steps needs to be broken down into elementary steps. This adds realistic details that mirror actual reaction pathways.

The simplest elementary reactions involve the dissociation of a diatomic molecule such as that of an H_2, and the combination of two free radicals such as the formation of an H_2 molecule. These reactions are fully characterized by their energies of dissociation.

It is not realistic to consider all elementary reactions as dissociations and combinations, because triatomic reactions could take place with lower activation energy than either reactant's dissociation energy. For instance, the collision of a chlorine free radical with a hydrogen molecule involves three atoms at one step: if the condition is right, it makes a hydrogen chloride at the same time as the original covalent bond between the two hydrogen atoms is broken. To form a HCl molecule, an electron transfers from the old H-H sigma bonding orbital to the new H-Cl one to pair with the free electron of the chlorine radical. This could happen with less energy than required to break the H-Cl or H-H bond. Furthermore, because the H-Cl bond is made at the expense of breaking the H-H bond, it is not appropriate to decompose this elementary step algorithmically into the dissociation of H_2 and the formation of HCl, which will be two uncorrelated sub-processes, be they subsequent or concurrent.

For a reaction that does not involve very complex changes in molecular structures, such as the free radical substitution reaction $A_2 + B_2 \rightleftharpoons 2AB$ (the double arrow $\rightleftharpoons$ means that the reaction is reversible in either way), the *n*-body elementary reactions ($n > 3$) that cannot be decomposed into diatomic and triatomic elementary reactions have low probability of occurrence, and can be neglected for simplicity.

To simulate a given type of reaction, rules for possible reaction pathways have to be coded. For example, the reaction $A_2 + B_2 \rightleftharpoons 2AB$ can be decomposed into the following five elementary steps[2]:

❏ Diatomic elementary reactions (dissociations and combinations terminating the chain reactions):

  o $A_2 \rightleftharpoons 2A\bullet$
  o $B_2 \rightleftharpoons 2B\bullet$
  o $A\bullet + B\bullet \rightleftharpoons AB$

  where $A\bullet$ and $B\bullet$ are free radicals and the dots represent unpaired electrons.

❏ Triatomic elementary reactions (bond-exchange reactions propagating the chain reactions):

- $A_2 + B\bullet \rightleftharpoons A\bullet + AB$
- $A\bullet + B_2 \rightleftharpoons AB + B\bullet$

In a simulation, these five steps are made to happen according to certain rules. In particular, the dissociations of A_2, B_2 and AB are all assumed to be homolytic fissions, regardless of what their local environments might be when the dissociations take place, in order to simplify the rules[3]. For each existing bond and group of atoms possible to form bonds, the critical conditions for these steps are checked according to the rules that will be discussed in the following subsection. To accelerate the critical condition search during a MD simulation, the same Verlet neighbor list used to compute the van der Waals forces *(11)* is used to check every possible pair of atoms in the system for collisions. If an elementary reaction satisfies its critical condition, the corresponding bond(s) will be made or broken.

The rules for diatomic and triatomic elementary reactions

There are two types of diatomic elementary reactions: breaking and making a bond. A bond is broken only when a bonded pair has sufficient energy to escape the potential well formed by its partner (see Fig. 1). The criterion for breaking a diatomic bond can be written as:

$$\mu_m^l + \frac{1}{2}k_m^l(l_m - l_m^0)^2 \geq 0 \qquad (l_m > l_m^0)$$

Here, μ_m^l is the chemical energy associated with the m-th bond, and k_m^l the radial spring constant associated with that bond. μ_m^l is a negative number, because the chemical energy of a non-bonded atom is assumed to be zero. The absolute value of this term is the energy required to break a bond. Satisfying these two inequalities requires that the vibrational potential energy in the bond be greater than the static chemical energy and that the bond be stretched, not compressed.

Bonded atoms can gain kinetic energy and convert it into the vibrational potential energy needed to break a bond from a collision with other atoms. At a given temperature, the more stable a chemical bond is, the larger $\left|\mu_m^l\right|$ is, and the less likely the bond will be broken. The probability of a bond breaking increases as the system's temperature rises, because more atoms will gain sufficient kinetic energy.

The computation assumes no barrier for two free radicals to combine. Formation of a molecule from two free radicals is always allowed because it reduces the potential energy of the system. Therefore, the rule for making a bond between two free radicals is simpler: whenever two free radicals collide, they will make a bond.
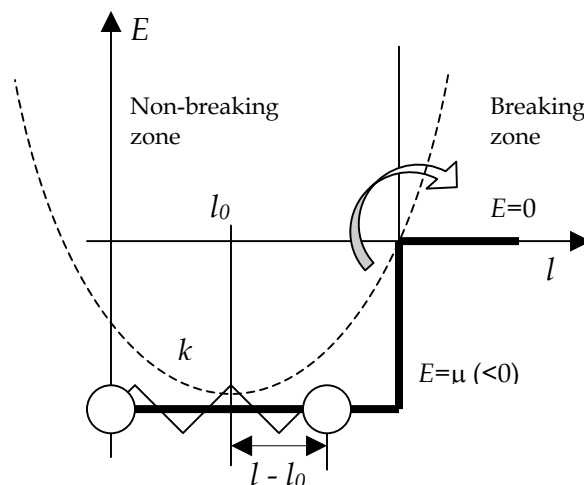
Fig. 1. A schematic illustration of the bond-breaking rule. The atoms, represented by circles, vibrate harmonically in the radial direction, l, around its zero position l_0. Its chemical energy at l_0 is μ, a negative number. The vibrational potential energy in the spring is $\frac{1}{2}k(l-l_0)^2$, represented as a dashed parabola. At a point to the right of l_0 that this parabola is greater than $|\mu|$ above its minimum, the atom has sufficient energy to break the bond. The bond is removed and $\mu + \frac{1}{2}k(l-l_0)^2$ is added to the kinetic energy of the two atoms.

A triatomic reaction such as A• + B$_2$ $\rightleftharpoons$ AB + B• involves an activation energy E_a along its reaction path. The model assumes that the energy needed to get over the activation energy potential barrier comes from the translational component of the relative kinetic energy along the line of centers of the colliding pair (see Fig. 2).

$$\frac{m_i m_j}{m_i + m_j} \times \frac{\left| (\vec{V}_i - \vec{V}_j) \cdot (\vec{R}_i - \vec{R}_j) \right|^2}{\left| \vec{R}_i - \vec{R}_j \right|^2} \geq E_a$$

Once such a critical condition is met, an A-B bond will be made between the colliding A-B pair and the original B-B bond will be broken. To keep the same potential energies, the positions of the atoms are not changed. The new AB molecule and B• radical will continue to move as determined by all the applicable forces, including the new bond. Due to the double-occupancy rule in quantum mechanics, if the A• has originally a valence electron, the B• radical is guaranteed to leave with one (assuming no excitation to the LUMO). Considering our previous assumption that all dissociations are homolytic fissions[3], no intermediate products like an atom without a valence electron, or one overloaded by two valence electrons at the LOMO, will be generated by these diatomic and triatomic elementary reactions.
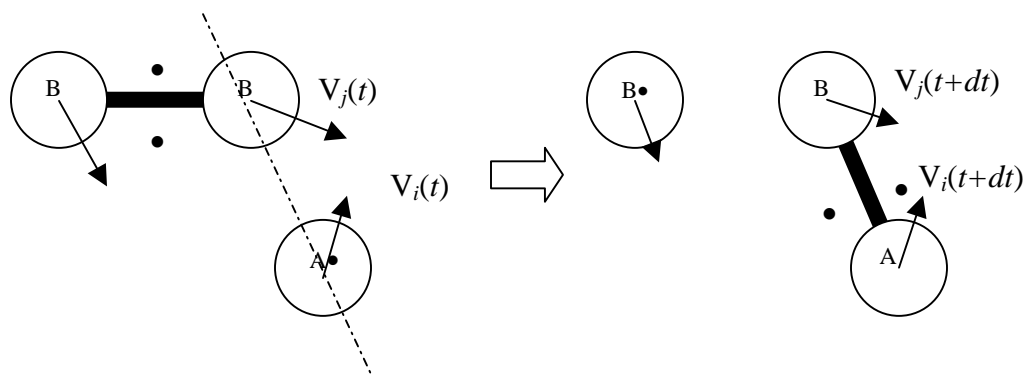
Fig. 2. A triatomic bond exchange reaction. If the head-on kinetic energy for the AB pair exceeds the activation energy E_a, the A-B bond is created and the B-B bond is broken. The dots stand for electrons. It is assumed that both A and B have only one valence electron in their free states.

The energy conservation constraint

Each elementary reaction must conserve energy. Breaking a bond eliminates the vibrational potential energy and the chemical energy. Similarly, creating a new bond adds these terms. In a triatomic reaction, one bond is broken and another made with different potential energies. If the change in the potential energy in an elementary reaction is negative, the kinetic energy of the reacting atoms must be increased by the same amount so that the total energy change is zero. If the potential change is positive, the kinetic energy of the reacting atoms must be decreased by the same amount. If the potential energy change cannot be compensated by reducing the kinetic energy of the reacting atoms, the reaction step is not permitted. When the reaction step is allowed, the velocities of the involved atoms are rescaled to increase or decrease their kinetic energy.

The energy conservation constraint is not simply an arbitrary way of conserving energy. It actually accounts for the energy exchange between potential and kinetic energy during each reaction, which results from a complex coupled electron-nucleus process. For example, in reality, the formation of a bond would result in a molecule in a lower potential energy state. The potential difference is converted into kinetic energy, thus increasing the temperature of the system. The breaking of a bond, on the contrary, absorbs kinetic energy and raises the system's potential energy to a higher level.

Simulation results

A common student misconception is the belief that a reaction ceases at equilibrium. Although each bond-making and bond-breaking event in our simulation can be set to unidirectional with certain parameters, these events can combine in a simulation to result in chemical reactions that can proceed in both directions and exhibit a dynamic equilibrium. Such a simulation can easily dispel the misconception about equilibrium by showing both a visual representation of the system and summary statistics. By generating a real-time display, the user sees the continuous making and breaking of bonds, while the statistical averages of the concentrations of reactants and products level off at a value that depends on the three dissociation energies (Fig. 3). From these data, the equilibrium constants can be estimated.
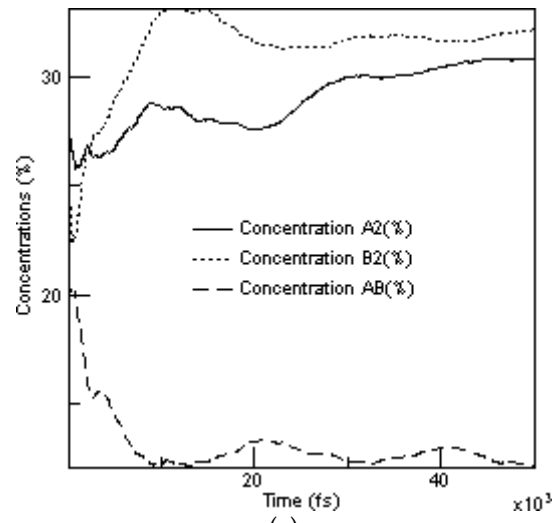
(a)
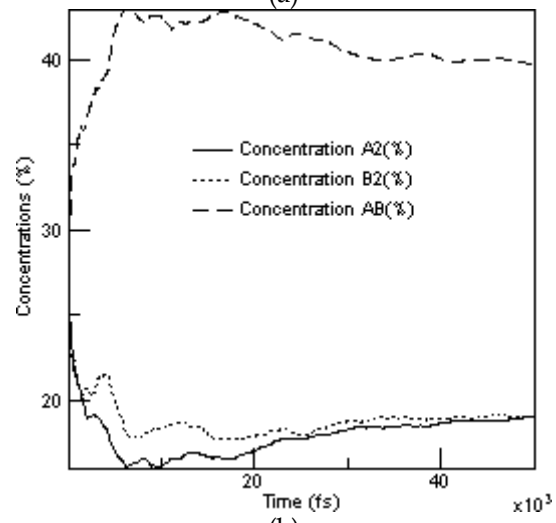
(b)
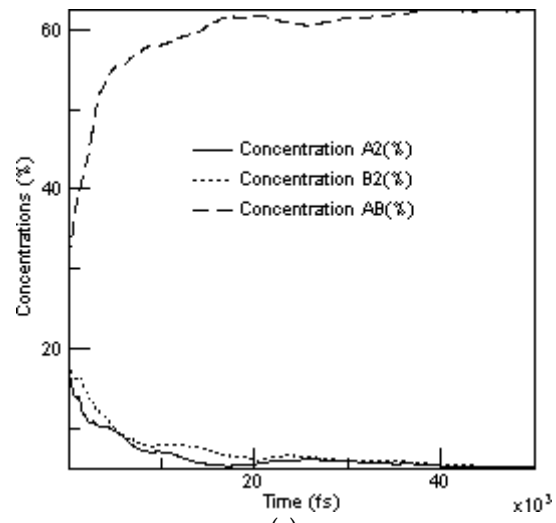
(c)

Fig. 3. The running averages of concentrations [A$_2$], [B$_2$] and [AB] of a 72-atom system (36 A and 36 B) recorded in 50-picosecond constant-volume-energy (NVE) MD simulations in three different situations. The three simulations all started from an identical initial condition (which was actually an equilibrated conformation of case b in the following), except that the dissociation energies of A$_2$, B$_2$ and AB are set to be: (a) 0.5, 0.5, 0.25 eV; (b) 0.5, 0.5, 0.5 eV; and (c) 0.25, 0.25, 0.5 eV. In the three simulations, the activation energies for the two bond-exchange reactions were both set to be 0.1 eV, which means the bond-exchange reactions are always favored over dissociations. The MD simulation shows that the running average concentrations in case b approximately converge to: [A$_2$]≈[B$_2$]≈[AB]/2, which conforms to a molar equilibrium constant K_c≈4, as expected. ([AB] is less than 50% of the total molecular weight in the system because there are always some free radical fragments).

Chemical explosions can be simulated by setting the level of the chemical energy stored in an A-B bond to be significantly lower (more negative) than those stored in A-A and B-B bonds. A system that begins with only A$_2$ and B$_2$ molecules can gain a lot of kinetic energy by creating AB molecules through the chain reactions. Fig. 4 shows a typical result of energy conversion under these conditions. As shown in Fig. 5, the explosion begins when one A$_2$ or B$_2$ molecule disassociates due to random energy fluctuations (Fig. 5c), and then one of the resulting free radicals forms the first AB molecule (Fig. 5d). This releases enough energy to initiate a chain reaction that creates more radicals and AB molecules.

Many of the properties of chemical explosions can be simulated with this system. For example, explosions caused by raising temperature, ignition, light-induced explosions, and explosions initiated by the introduction of a few free radicals, can be modeled.
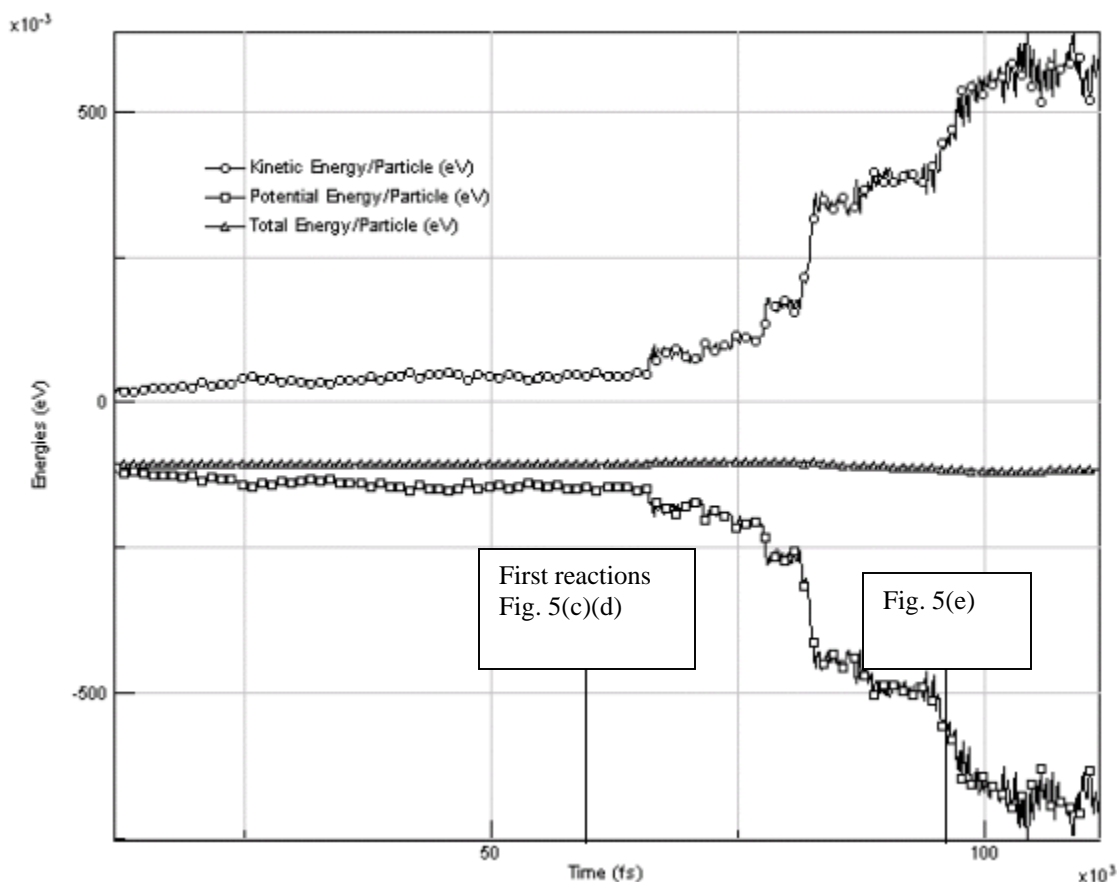
Fig. 4. Energy curves produced in an explosion simulation. The drastic change of kinetic and potential energies can be shown in a MD simulation of a chemical explosion. This also uses the $A_2 + B_2 \rightleftharpoons 2AB$ system, but here the dissociation energy for AB is much larger than those for A_2 and B_2. You may notice that energy conservation is not perfect in the explosion phase. This is because the numerical errors increase with drastically rising temperature. Reducing the time step of MD integration would decrease the errors.
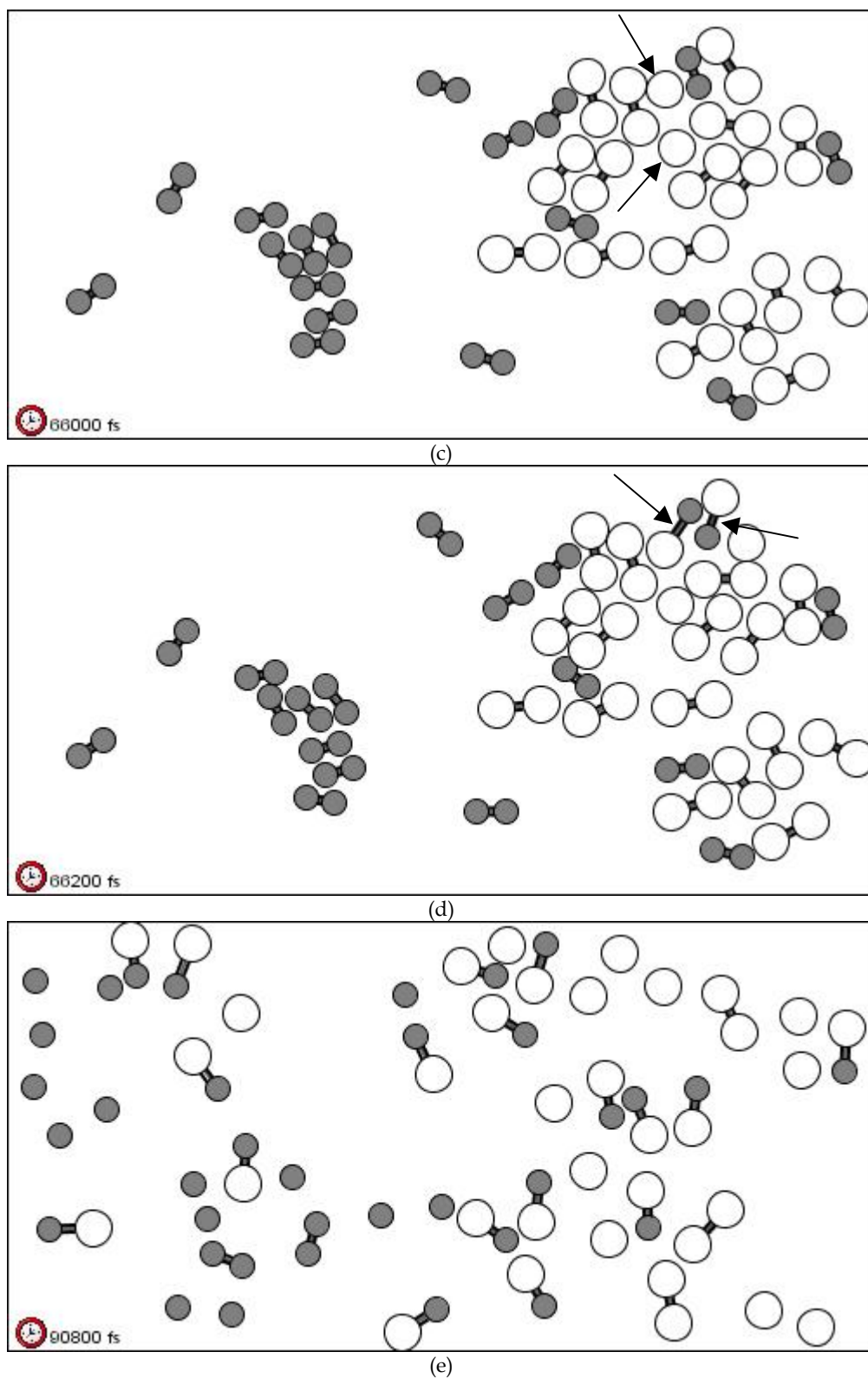

(a)

(b)

(c)

(d)

(e)
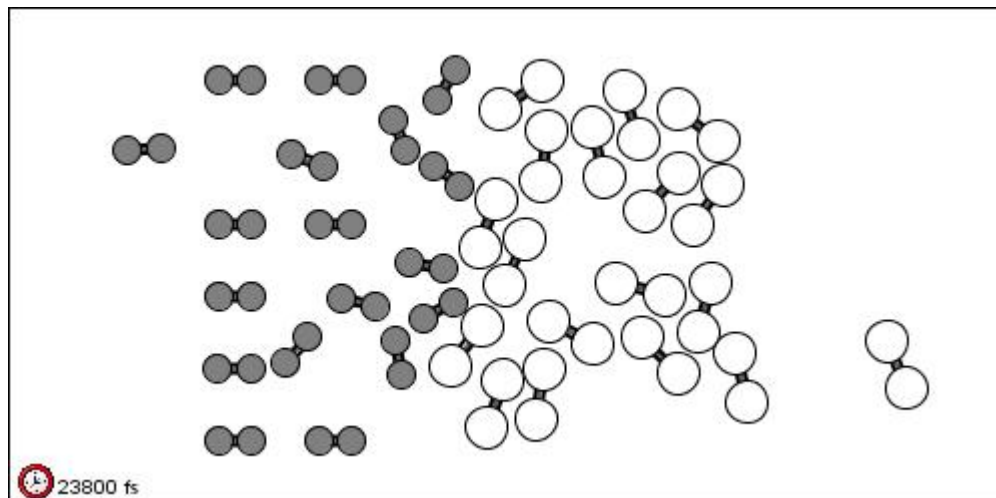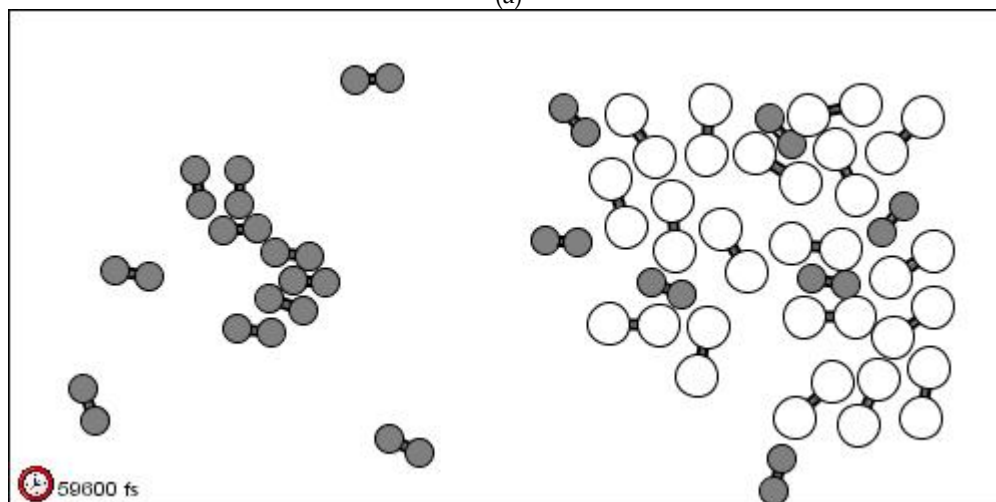
Fig. 5. A few snapshots from the explosion simulation of Fig. 4. (a) A_2 (the gray circles) and B_2 (the white circles) come into contact. (b) Through diffusion, A_2 and B_2 mix. Because A_2 is lighter than B_2, some A_2 molecules manage to squeeze into the open space among B_2 molecules. (c) A B_2 molecule

breaks apart, creating two B• free radicals shown by arrows. (d) One of the B• free radicals hits a nearby A_2 and produces an AB molecule and an A• radical. The A• radical hits a B_2 next to it right away, and generates another AB molecule and a B• radical. The two AB molecules are pointed out by arrows. All these reactions take place in 200 femtoseconds. (e) A snapshot taken roughly 24 picoseconds after the first dissociation. Notice that at this point, there are 18 AB molecules and many free radicals. Fig. 4 indicates that the temperature of the system has increased drastically.

A homogenous catalyst

Catalysis is a core concept for chemistry and biology, but students are seldom given a mechanistic explanation for it. The Molecular Workbench provides a homogenous catalysis of a tri-molecular form: $A_2 + B_2 + C \rightleftharpoons 2AB + C$ (where C is the catalyst), which is based on the bi-molecular reaction $A_2 + B_2 \rightleftharpoons 2AB$ discussed in the previous sections and has a reaction mechanism similar to that of ozone destruction reaction catalyzed by chlorofluorocarbons. This simple model can help students understand the atomic-scale level causes of a typical homogenous catalysis. This simulation also demonstrates that a catalyst can catalyze many reactants, because it keeps on being regenerated through the chain reactions. This should help students understand why catalysts are not consumed in a catalyzed reaction.

To model a homogenous catalysis, the dissociation energies of the molecules A_2 and B_2, and the activation energies of the chain propagation reactions $A_2 + B• \rightleftharpoons A• + AB$ and $A• + B_2 \rightleftharpoons AB + B•$, are set so high that these elementary reactions have vanishing probability at the initial temperature. A new species of particle, C, is introduced. C does not react with other C particles but is able to react with both A_2 and B_2, through two sets of chain propagation reactions (Fig. 6). If these have lower activation energies than the activation energies of the original pathway, the reaction can proceed through the new pathways, as shown in Fig. 7.

This catalytic reaction has been simulated using an algorithm similar to that of the $A_2 + B_2 \rightleftharpoons 2AB$ reaction. The difference is that searching the critical conditions in this reaction algorithm is more complicated, and the controlling parameters are more than doubled (11 compared to 5).
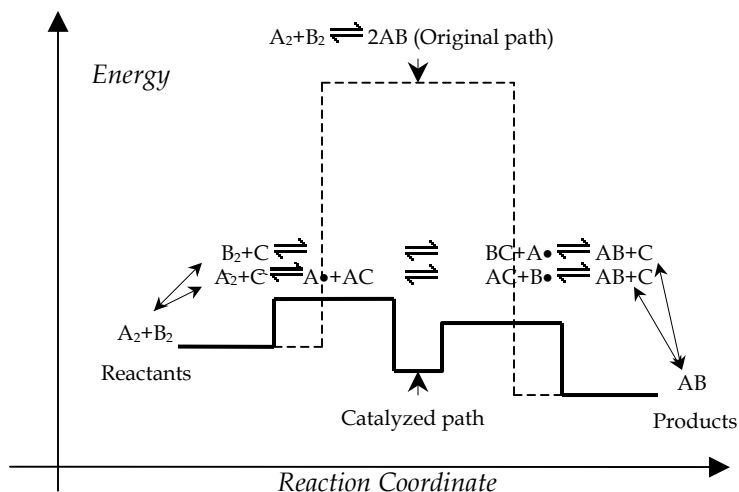

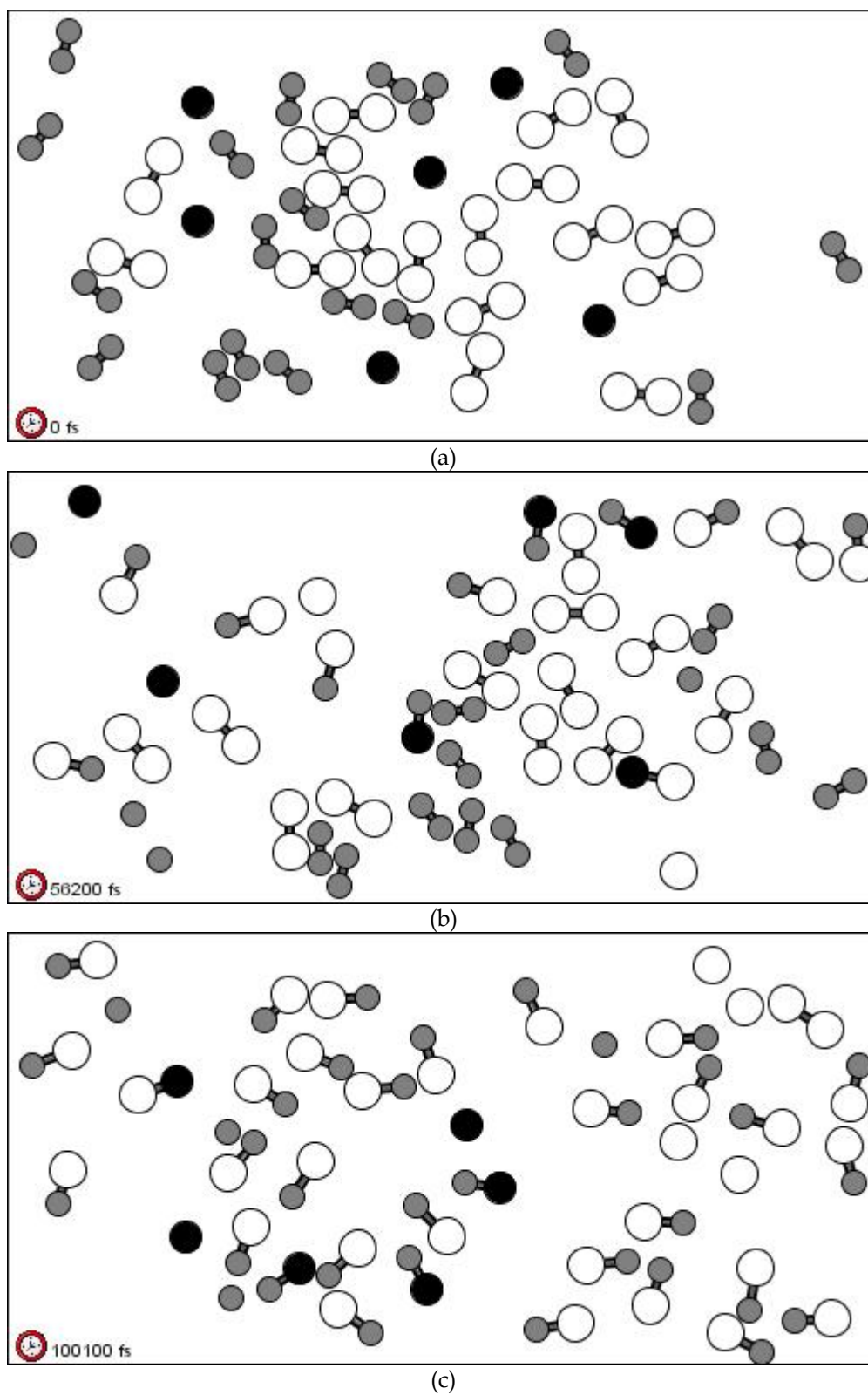Fig. 6. Catalyst C provides two alternative pathways that have lower activation energies.

Fig. 7. Snapshots of a simulation of the catalyzed reaction $A_2 + B_2 + C \rightleftharpoons 2AB + C$ under the constant-volume-energy (NVE) condition. (a) Initially, six C catalysts (represented by solid black circles) were added to a system of A_2 (gray circles) and B_2 (white circles) molecules that were unable to react

directly. (b) At an intermediate frame, AC, BC and free A and B radicals have been produced. (c) About 100 picoseconds later, most of A_2 and B_2 were converted to AB molecules.

Concluding remarks

This paper reports a method of simulating chemical reaction kinetics by adding rule-based elementary reactions to a MD simulation. Two abstract types of reactions, $A_2 + B_2 \rightleftharpoons 2AB$ and $A_2 + B_2 + C \rightleftharpoons 2AB + C$, are given as examples. Each type is characterized by a simple set of parameters that govern the reaction, and may be mapped to different types of real reactions by adjusting the parameters. For example, $A_2 + B_2 \rightleftharpoons 2AB$ may be used to model the reactions between hydrogen and halogens, with a different set of parameters for a different type. The method could be generalized to other types of substitution reactions such as $AB + CD \rightleftharpoons AC + BD$, or addition reactions such as $AB + C \rightleftharpoons ABC$.

Although the method can produce much of the chemical reaction kinetics, there are several limitations that need to be pointed out. First, we chose to restrict our simulations to 2D, because 2D displays are easier to understand and analyze than 3D ones. The drawback is that the model cannot be used to simulate reactions fundamentally determined by 3D molecular structures. Second, because our computational model is a combination of MD and rules, it is *not* intended to predict reactions or to simulate arbitrary chemical reactions. Our goal is primarily to support a limited number of simple chemical reactions that student can explore. Third, it does not address many important aspects of chemical reactions. For example, how the electronegativity of the reactants affects the overall reaction (charges and electron/proton transfer processes) is not taken into consideration. Furthermore, it also does not correctly account for entropy change in reactions for several reasons: the dimensionality, the complete neglect of such elementary reactions as $AB + A \rightleftharpoons A + AB$ that do not yield a net change[2], and the 100% probability of bond formation and breaking whenever there is sufficient energy.

Nevertheless, the capacity of the method has many potential applications for learning the core concepts of chemistry. The connections between atomic-scale interactions, activation and dissociation energies, elementary reactions, chemical equilibria, and temperature are difficult for students to understand. At the root of these difficulties is the fact that many of the macroscopic phenomena emerge from the interactions of large numbers of atoms. While beginning students might understand the basic physics of these interactions, they lack the mathematical skills to understand the relationship between the atomic-scale physics and the emerging macroscopic chemistry. The only formal way to derive the macroscopic behavior of such systems is through rather sophisticated statistical mechanics. The molecular models delivered by the Molecular Workbench software provide a different, more accessible route to understanding.

Note

1. The decomposition of electronic energy into two- and three-center terms does not work for degenerate systems such as the benzene molecules, which have delocalized molecular orbitals.
2. There exist many other possible elementary reactions, such as $A_2 + A\bullet \rightleftharpoons A\bullet + A_2$ or $AB + A\bullet \rightleftharpoons A\bullet + AB$. These steps do not cause a net change to the reacting systems, and are therefore ignored in the implementation.
3. Had heterolytic fissions been taken into account, we would have had to distinguish among atoms of the same type as those with no valence electron, those with one valence electron, and those with two valence electrons. This would greatly complicate the rules. For instance, if two colliding atoms both have no valence electron, or both have two valence electrons, no bond should be made between them; only those that satisfy the double-occupancy rule will be allowed to make a bond.

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