

## MOLECULAR DYNAMICAL STUDY OF THE ENERGY RELAXATION PROCESSES AFTER HEATING THE VIBRATIONAL DEGREE OF FREEDOM IN A DIATOMIC MOLECULAR CRYSTAL\*

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**ABSTRACT:** Energy relaxation processes initiated by sudden heating of the vibrational degree of freedom were studied with molecular dynamical method. A unit cell of bcc structure containing 128 diatomic molecules with periodic boundary conditions was considered. Compound Morse potential was assumed as the atom-atom interactions. It was found that the logarithm of the equilibration time depends linearly upon a factor  $f_{21}$  which is proportional to the frequency ratio of the intra- and inter-molecular vibrations.

**KEY WORD:** molecular dynamics, relaxation, molecular crystal.

### I. INTRODUCTION

Energy relaxation processes exist in a variety of physical phenomena, e.g., fluid flow, sound propagation, shock wave, detonation. These processes result from the finite rates of energy transfer among various degrees of freedom of the molecules: translational, vibrational and rotational. For this reason, when a system is disturbed, energy equilibration within the system is not reached instantaneously and requires relaxation processes. The effect of these relaxation processes must be taken into account when the time scale of the macroscopic process is comparable with the relaxation times. In general, the energy relaxation processes are affected by the intra- and inter-molecular interactions of the molecules<sup>[1]</sup>. Therefore, the investigation of the effects of the atom-atom interactions on the relaxation processes is an important subject of molecular dynamics

There are several advantages in using the molecular dynamical method for investigating the relaxation processes. Firstly, the relaxation times can be calculated directly without the need of building a statistical model. Secondly, it is possible to heat the individual degrees of freedom selectively. Thirdly, the details of the energy transfer processes can be "measured" from the motion of the atoms.

In this article we present a molecular dynamical study of the relaxation processes in a diatomic molecular crystal in which the vibrational degree of freedom are rapidly heated. We examine the relationship between equilibration time and the parameters of the atom-atom potentials.

### II. BASIC PHYSICAL MODEL AND PROCEDURE OF CALCULATION

#### 1. Scheme of computer experiment

Our model is a diatomic molecular system similar to that described in [1]. It has been initially

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prepared in equilibrium before the kinetic energy is added to the vibrational degree of freedom. The subsequent redistribution of the energies in the vibrational, rotational, and translational degrees of freedom will be used to determine the relaxation (or equilibration) times.

## 2. Physical model

The basic features of the model are similar to those of ref.[1]. We have 128 diatomic molecules in a cube of  $4 \times 4 \times 4$  bcc unit cell with periodic boundary conditions in three dimensions. The initial velocities of the atoms are given randomly, and are taken quite low so that the molecules will not dissociate after heating.

## 3. Atom-atom potentials

As in [1], we use a compound Morse potential:

$$V_1(r) = \varepsilon \left\{ \exp[2a_1(1-r/r_m)] - 2\exp[a_1(1-r/r_m)] \right\} \quad \text{for atoms of two different molecules} \quad (1a)$$

$$V_2(r) = b_2\varepsilon \left\{ \exp[2a_2(c_2-r/r_m)] - 2\exp[a_2(c_2-r/r_m)] \right\} + Q \quad \text{for atoms within a molecule} \quad (1b)$$

where  $V_1$  and  $V_2$  are the pair interaction potentials;  $r$  is the distance in the atom pair;  $\varepsilon$  is the well depth of  $V_1$ ;  $r_m$  is the position of its minimum;  $a_1, a_2, b_2, c_2$  are constants; and  $Q$  is the exothermicity parameter.  $a_1$  and  $a_2$  are related to the steepness of the potentials,  $b_2$  is the dimensionless well depth of  $V_2$  and  $c_2$  the dimensionless position of its minimum.

$a_1$  and  $a_2$  control the inter- and intra-molecular frequencies of oscillation. In our calculations we make these frequencies not too different from one another in order to enhance the intermolecular coupling and, hence, the energy exchange among the molecules. This results in less consumption of computer time that is an important practical advantage (see ref.[1]). We also make  $b_2$  large enough to prevent the molecules from dissociation so that only the energy relaxation processes can be observed after heating. For the same reason,  $Q=0$  is assumed. We make  $c_2=a_1/a_2$  for convenience. The parameters used in our calculations are listed in Table 1.

## 4. Equations of motion

We use natural units for the system:  $\varepsilon$  for unit of energy,  $r_m$  for unit length and  $m$  for unit of mass. Then, the unit of force is  $\varepsilon/r_m$ , and the unit of time is  $r_m\sqrt{m/\varepsilon}$ . From Eq.(1) the dimensionless potentials can be written as:

$$U_1(R) = \exp[2a_1(1-R)] - 2\exp[a_1(1-R)] \quad (2a)$$

$$U_2(R) = b_2 \left\{ \exp[2a_2(c_2-R)] - 2\exp[a_2(c_2-R)] \right\} \quad (2b)$$

Then the resultant force on the  $i$ -th atom may be written as

$$\mathbf{F}_i = -\text{grad}_i \sum_{j \neq i} U(\mathbf{R}_{ij}) \quad (3)$$

and the equation of motion as

$$d^2\mathbf{R}_i/dt^2 = \mathbf{F}_i \quad (4)$$

where  $U$  represents either  $U_1$  or  $U_2$  depending on whether the atom pair  $i$  and  $j$  belongs to the different or same molecules.

We solve equations (4) by the Newton-Cauchy method, with a time step of 0.01 and thus obtain the motion of all the particles and their average kinetic energies in the vibrational, rotational, and translational degrees of freedom at each time step. These kinetic energies are further averaged over a number of time steps. The evolution of these averages as a function of time provides information on

the interested relaxation processes.

### 5. Initial equilibrium state

Before heating, we run the system according to equations (4) for a long period of time to ensure that the system has reached an initial state of equilibrium. Since the motion of the atoms is controlled by the potentials (2a) and (2b), the equilibrium must be reestablished for each run to which a new group of constants  $a_1$ ,  $a_2$ ,  $b_2$ , and  $c_2$  are given. The system is considered to be in equilibrium when it deviates from energy equipartition by less than a prescribed amount (0.01). In general, a total amount of 5 to 25 units of time is required for obtaining the pre-equilibration state of the system.

### 6. Heating

The method of heating vibrational degree of freedom is as follows. The velocity components of the two atoms of a molecule are denoted as  $(u_{x1}, u_{y1}, u_{z1})$  and  $(u_{x2}, u_{y2}, u_{z2})$  in the laboratory coordinates. These can be transformed into those in the molecular coordinates  $(x', y', z')$  by using Euler's angles coordinate transformation:

$$\begin{aligned} v_{x1} &= u_{x1} \cos\theta \cos\varphi + u_{y1} \cos\theta \sin\varphi - u_{z1} \sin\theta \\ v_{y1} &= -u_{x1} \sin\varphi + u_{y1} \cos\varphi \end{aligned} \quad (5a)$$

$$\begin{aligned} v_{z1} &= u_{x1} \sin\theta \cos\varphi + u_{y1} \sin\theta \sin\varphi + u_{z1} \cos\theta \\ v_{x2} &= u_{x2} \cos\theta \cos\varphi + u_{y2} \cos\theta \sin\varphi - u_{z2} \sin\theta \\ v_{y2} &= -u_{x2} \sin\varphi + u_{y2} \cos\varphi \end{aligned} \quad (5b)$$

$$v_{z2} = u_{x2} \sin\theta \cos\varphi + u_{y2} \sin\theta \sin\varphi + u_{z2} \cos\theta$$

where we take the line through the two atoms as the  $z'$  axis in the new coordinates;  $x'$  and  $y'$  are arbitrary;  $\theta$  and  $\varphi$  are two Euler's angles. Then, the translational, rotational, and vibrational kinetic energies are given in terms of the velocity components in the new coordinates as:

$$\begin{aligned} E_t &= [(v_{x1} + v_{x2})^2 + (v_{y1} + v_{y2})^2 + (v_{z1} + v_{z2})^2] / 12 \\ E_r &= [(v_{x1} - v_{x2})^2 + (v_{y1} - v_{y2})^2] / 8 \\ E_v &= (v_{z1} - v_{z2})^2 / 4 \end{aligned} \quad (6)$$

It can be seen from these formulas that if the components  $v_{z1}$ ,  $v_{z2}$  are changed to  $v'_{z1}$ ,  $v'_{z2}$  according to

$$v'_{z1} - v'_{z2} = \alpha_v (v_{z1} - v_{z2}) \quad v'_{z1} + v'_{z2} = v_{z1} + v_{z2} \quad (7)$$

and, at the same time,  $v_{x1}$ ,  $v_{x2}$ ,  $v_{y1}$  and  $v_{y2}$  are kept unchanged,  $E_v$  is increased by a factor of  $(\alpha_v)^2$ , while  $E_t$  and  $E_r$  remain unchanged.

Replacing  $v_{z1}$  and  $v_{z2}$  in (5) with  $v'_{z1}$  and  $v'_{z2}$  and solving for  $u_{x1}$ ,  $\dots$ ,  $u_{z2}$  on the right side of (5), we can obtain the velocity components which correspond to the kinetic energies after  $(\alpha_v)^2$  time heating of the vibrational degree of freedom.

## III. RESULTS AND DISCUSSION

We have carried out calculations with six groups of potential parameters listed in Table 1. The results shown in Figs. 2 and 3 for the third and sixth groups are typical. In these figures, the data on the left of point  $A$  (omitted in Fig. 2) show the pre-process for establishing initial equilibrium. The data on the right of point  $A$  show the relaxation processes after the vibrational degree of freedom is heated. Here we see the sharing of the vibrational kinetic energy with the rotational and translational energies. As the energies in these degrees of freedom tend toward equilibrium, the results show that

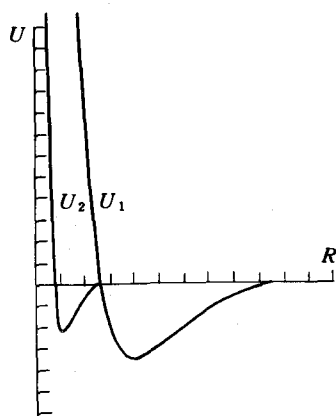
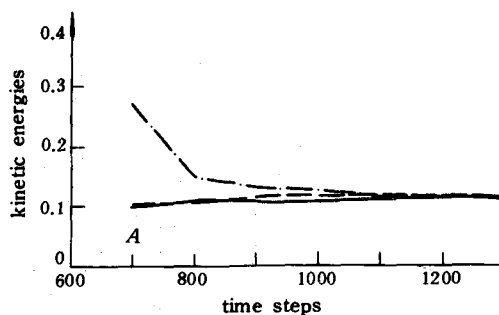


Fig.1 Compound Morse potential

Fig.2 Energy relaxation processes at  $f_{21} = 2.828$ 

— vibrational — rotational — translational

the energy transfer processes require finite times, i.e., the results give a direct measurement of the relaxation times for the different degrees of freedom. The equilibration time in Fig.2 is much shorter than that in Fig.3 due to the differences in the potential constants in the two cases. The equilibration times in the six cases are listed in the last column of Table 1.

Table 1

Conditions and results in six cases

No.	$a_1$	$a_2$	$b_2$	$c_2$	$\alpha_v$	$f_{21}$	$T$
1	1.9804	6.0331	0.66	0.3283	1.7321	2.475	280
2	1.9804	6.8950	0.66	0.2872	2.0000	2.828	300
3	1.9804	6.8950	0.66	0.2872	1.7321	2.828	300
4	1.9804	5.6015	1.00	0.3536	2.2500	2.828	300
5	1.9804	9.7509	0.66	0.2031	1.4142	4.000	850
6	1.9804	9.7509	1.32	0.2031	3.0000	5.657	2900

Comparing cases 2 and 5, we see that the equilibration time for case 5 (850) is much longer than that in case 2 (300), only because the constant  $a_2$  in case 5 is larger. This shows that when  $U_2$  is steep, energy transfer from vibration to rotation and translation is difficult. The steepness of  $U_2$  can also be increased by increasing  $b_2$ , as in case 6 (comparing with case 5). Here we see that the equilibration time in case 6 (2900) is also much longer than that in case 5.

It is of interest to note that the effects of  $b_2$  and  $a_2$  on the equilibration time can be compensatory. For example, the equilibration times in cases 3 and 4 are the same, but their  $b_2$  and  $a_2$

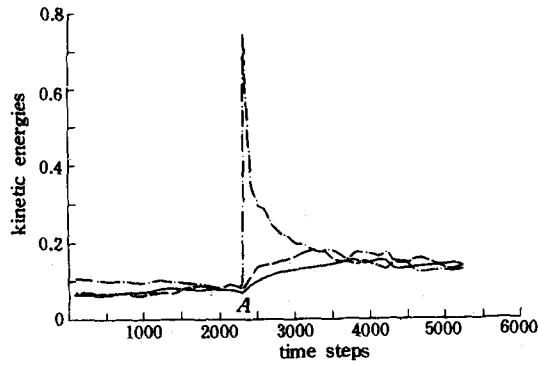


Fig.3 Energy relaxation processes at  $f_{21}=5.657$

----- vibrational ----- rotational ----- translational

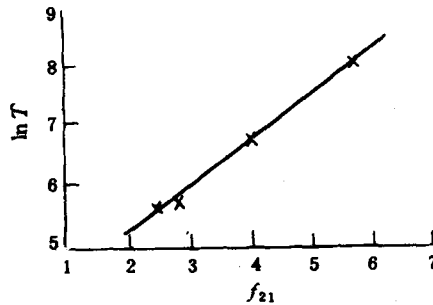


Fig.4 Equilibration time vs. frequency factor

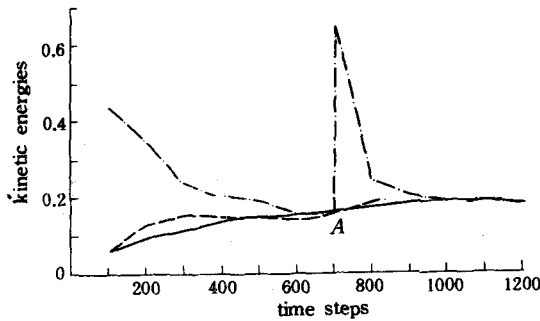


Fig.5 Energy relaxation processes for stronger heating at  $f_{21}=2.828$

----- vibrational ----- rotational ----- translational

are different. However, in both cases, the constants  $a_2 \sqrt{b_2}$  are equal. We know that the ratio of the frequencies of the intra- and inter-molecular vibrations is important in determining the intermolecular coupling [1]. This ratio may be shown by dimensional analysis to be proportional to a factor:

$$f_{21} = (\sqrt{\epsilon_2}/r_{m2})/(\sqrt{\epsilon_1}/r_{m1}) = \sqrt{b_2}/c_2 = a_2 \sqrt{b_2}/a_1 \quad (8)$$

Therefore, certain functional relationship between equilibration time  $T$  and the frequency factor  $f_{21}$  must exist. In fact, it is a linear function between  $\ln T$  and  $f_{21}$  (see Fig.4).

In addition, from cases 2 and 3, we see that at the same value of  $f_{21}$  but with different  $\alpha_v$ ,

approximately the same equilibration times are obtained. This means that the equilibration time is independent of the amount of heat added.

Finally, Figs. 2, 3, and 5 all show that the rotational energy increases more rapidly after heating than the translational. This means that energy transfer from vibrational to rotational degree of freedom is easier than that to translational degree of freedom. These problems will be studied in the future.

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#### REFERENCES

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