Semiclassical dynamics of shock wave propagation in molecular crystals: application to the Morse lattice

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Abstract. The semiclassical cluster model for the propagation of shock waves in solids is applied to a linear molecular lattice witth Morse interaction potentials. The exact quantum eigenstates for a cluster are first found and the interactions between neighbouring clusters are then considered as time-dependent perturbations which induce transitions among the cluster eigenstates. Calculations using the semiclassical cluster model qualitatively agree with classical calculations, although quantitative differences do arise in the atomic coordinates and molecular energies because of the anharmonity of the potentials.

1. Introduction

For the past few decades, the propagation of shock waves in condensed matter has been extensively investigated [1–3] with a variety of experimental techniques. However, theoretical studies are very difficult due to the large number of degrees of freedom. Most theoretical investigations have been based upon numerical integration of the classical equations of motion [4–22] for harmonic or anharmonic 1D, 2D, or 3D atomic or molecular lattices. A few approximate quantal studies have been reported [23–27], some of which make restrictive approximations, including the propagation of Gaussian wavepackets.

Recently, Marston and Wyatt developed a semiclassical method for investigating shock wave propagation in molecular lattices [28]. In the cluster model, a group of molecules are selected for investigation using quantum mechanical methods. The dynamics of molecules within the cluster are found by integrating quantum mechanical equations of motion for the state amplitudes, after a time dependent perturbation $V(t)$ is 'turned on.' This perturbation allows the shock wave to enter through one edge of the cluster and then leave, at a later time, through the opposite edge.

So far, the cluster model has been applied only to harmonic or cubic anharmonic linear diatomic lattices. The cluster was defined to include two diatomic molecules and all four degrees of freedom were treated quantum mechanically.

In this study, the cluster model is applied to a linear diatomic lattice with Morse interaction potentials. The whole lattice is partitioned into a series of clusters and the quantal solutions for each cluster are found. Interactions between different clusters are considered as time-dependent perturbations. Translation of the centre-of-mass of each cluster is treated classically, while the intermolecular and intramolecular vibrational degrees of freedom are treated quantum mechanically. Particular emphasis is placed

Table 1. Parameters in Morse potentials†.

$m = 25\,538.58$ amu	$D_M = 0.358\,8235\,E_H$
$r_M = 2.071\,A_0$	$D_c = 0.014\,E_H$
$r_c = 6.213\,a_0$	$D_n = 0.036\,E_H$
$r_n = 4.142\,a_0$	$A = 0.6\,E_H$
$\beta_M = \beta_c = \beta_n = 1.433\,7845\,a_0^{-1}$	$\alpha = 1.0\,a_0^{-1}$

† E_H = Hartree energy unit, a_0 = atomic unit of length.

upon computation of the coordinates of the atoms in each cluster, the total energy of the cluster, and the energy for each molecule within the cluster.

2. Classical trajectory calculations

In this study, we consider a linear lattice of forty atoms which form twenty diatomic molecules. All atoms in the chain are of equal mass, that of a nitrogen atom, and the intramolecular potential is chosen as that of diatomic nitrogen for which a Morse potential has been used: $V_M(r) = D_M\{1 - \exp[-\beta_M(r - r_M)]\}^2 - D_M$, where r is the interatomic distance. The Morse potential parameters D_M, β_M and r_M are given in table 1. We separate the interaction potential between two molecules into two parts: one is a pairwise potential between neighbour atoms of the two neighbour molecules; another is an interaction potential between the centre of mass of the two molecules. Both potentials are chosen as Morse potentials. The Morse parameters D_n, β_n and r_n are for the pairwise nearest-neighbour potential and D_c, β_c and r_c refer to the centre-of-mass component.

In order to initiate the shock wave, a ballistic particle (impact atom) with mass equal to one of the chain atoms interacts with the chain through an exponential repulsive potential. The interaction potential between the impact atom and the first atom in the chain is given by:

$$V_{int}(q_1, q_0) = A\,e^{-\alpha(q_1 - q_0)} \tag{1}$$

where A and α are also given in table 1. As a result, the potential for the whole system is given by

$$V = \sum_{j=1}^{20} V_M(q_{2j} - q_{2j-1}) + \sum_{j=1}^{19} V_n(q_{2j+1} - q_{2j})$$

$$+ \sum_{j=1}^{10} V_c[\tfrac{1}{2}(q_{2j+2} + q_{2j+1} - q_{2j} - q_{2j-1})] + V_{int}(q_1, q_0). \tag{2}$$

Here, $\{q_i\}$ are coordinates of the ballistic particle and the atoms of the chain, V_M are the Morse potentials for diatomic molecules, V_n are the pairwise Morse potentials between neighbouring molecules, V_c are the Morse potentials between the centres-of-mass of two molecules and V_{int} is the potential between impact particle and the first atom in the chain.

Given this potential, Hamilton's equations were integrated numerically for specified initial conditions. Different initial conditions were used to initiate the trajectory calculations and the results were very close. As a result, the following simple set of initial conditions was used.

All atoms are initially at equilibrium, and the impact atom starts at a large distance from the first atom of the chain. The initial momenta can be calculated as following:

$$(P_2 - P_1)^2/_{2\mu} = \hbar\omega(n + \tfrac{1}{2}) - (\hbar^2\omega^2/4D_M)(n + \tfrac{1}{2})^2$$
$$n = 0, \mu = m/2, \omega = (\beta_M/2\pi)\sqrt{2D_M/\mu}. \tag{3}$$

Here, P_1 and P_2 are the momenta for two atoms in the molecule and we assume at $t = 0$ that $P_1 = -P_2$. This leads to the initial momenta:

$$P_i = (-1)^i[\tfrac{1}{4}\mu\hbar\omega(1 - \hbar\omega/8D_M)]^{1/2}. \tag{4}$$

In order to compare the classical and semiclassical results, for each cluster we define the origin of coordinates at the centre of mass of the cluster at the initial time and the trajectories of the four atoms of the cluster, q_1, q_2, q_3, q_4, are then computed. The mode energy of each diatomic molecule is calculated:

$$E_{\mathrm{mode}} = (P_2 - P_1)^2/2\mu + V_M(q_2 - q_1) \tag{5}$$

where, as before, P_1 and P_2 are the momenta of the two atoms in the molecule and V_M is the Morse potential for the molecule. The classical energy of the cluster is defined by:

$$E = \sum_{i=1}^{4} \frac{P_i^2}{2m} + V_M(q_2 - q_1) + V_M(q_4 - q_3) + V_M(q_3 - q_2)$$
$$+ V_c[\tfrac{1}{2}(q_4 + q_3 - q_2 - q_1)]. \tag{6}$$

3. Formulation of cluster model

After selecting a segment of the lattice which contains a small number of molecules, we partition the total time-dependent cluster Hamiltonian

$$H = H_c^0 + V_1(t) = (T + V_0) + V_1(t) \tag{7}$$

where H_c^0 is the time-independent cluster Hamiltonian, and $V_1(t)$ couples molecules within the cluster to those in neighbouring clusters. We then solve for the cluster eigenstates

$$H_c^0 \psi i = E_i\psi_i \qquad i = 1, 2 \ldots N \tag{8}$$

and use these as a basis for expanding the time-dependent wavefunction for the perturbed cluster

$$\Psi(t) = \sum_{i=1}^{N} c_i(t)\Psi_i. \tag{9}$$

The amplitudes $c_i(t)$ are solutions to the system of first-order coupled differential equations

$$i\hbar \frac{dc_i}{dt} = E_i c_i + \sum_{j=1}^{N} c_j\langle\Psi_i|V_1(t)|\Psi_j\rangle. \tag{10}$$

As an example, we will now consider a cluster containing two diatomic molecules,

in which all atoms have the same mass, m. In terms of Cartesian coordinates $\{q_i\}$, the Jacobi coordinates are

$$r_1 = q_2 - q_1 \qquad r_2 = q_4 - q_3$$

$$\rho = \tfrac{1}{2}[(q_3 + q_4) - (q_1 + q_2)] \qquad R = \tfrac{1}{4}[q_1 + q_2 + q_3 + q_4] \qquad (11)$$

where R is the centre-of-mass coordinate, ρ is the intermolecular displacement, and r_i are molecular vibrational coordinates for molecules labeled 1 and 2. The cluster Hamiltonian operator is then

$$H_c^0 = \frac{-\hbar^2}{2}\left(\frac{1}{M}\frac{\partial^2}{\partial R^2} + \frac{1}{\mu_1}\frac{\partial^2}{\partial r_1^2} + \frac{1}{\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{1}{\mu}\frac{\partial^2}{\partial \rho^2}\right) + V_0(r_1, r_2, \rho) \qquad (12)$$

where $M = 4m$, $\mu_1 = \mu_2 = m/2$, and $\mu = m$. We are assuming that the cluster potential—before the shock wave enters the cluster—is independent of the centre-of-mass coordinate. In addition, we will assume that the motion of the centre of mass, for the perturbed cluster, can be treated classically.

As a result of these restrictions, the stationary states of the cluster are determined by the Schrödinger equation,

$$\left[\frac{-\hbar^2}{2}\left(\frac{1}{\mu_1}\frac{\partial^2}{\partial r_1^2} + \frac{1}{\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{1}{\mu}\frac{\partial^2}{\partial \rho^2}\right) + V_0(r_1, r_2, \rho)\right]\Psi_i(r_1, r_2, \rho) = E_i\Psi_i(r_1, r_2, \rho).$$
$$(13)$$

The potential is now decomposed into

$$V_0(r_1, r_2, \rho) = V_M(r_1) + V_M(r_2) + V_n(\rho - \tfrac{1}{2}r_1 - \tfrac{1}{2}r_2) + V_c(\rho). \qquad (14)$$

In order to solve (13), we will expand the wavefunction in a direct product of Morse oscillator eigenstates,

$$\Psi_i(r_1, r_2, \rho) = \sum_{jkl} d_{jkli}\phi_j(r_1)\phi_k(r_2)\phi_l(\rho) \qquad (15)$$

where the eigenvectors d_i are found by diagonalizing the matrix representation of the cluster Hamiltonian in the Morse oscillator product basis.

4. Time-dependent perturbation potentials

If the Cartesian coordinates of the four atoms in a cluster are denoted q_i, q_{i+1}, q_{i+2}, and q_{i+3}, then the Jacobi coordinates r_i, r_{i+1}, ρ_i, and R_i are easily computed. The Cartesian coordinates of the two atoms in 'front' of the cluster are q_{i-2} and q_{i-1}, while q_{i+4} and q_{i+5} denote the coordinates of the two atoms 'behind' the cluster. From classical mechanics applied to the shocked lattice, we find the time dependence of the atoms in the two neighbouring clusters, $q_{i-2}(t), q_{i-1}(t), q_{i-4}(t)$, and $q_{i+5}(t)$. The time-dependence of these coordinates, in turn, produces time-dependence in the four intercluster poten-

tials involving the two nearest neighbour distances $\rho_{i-1}(t)$ and $\rho_{i-1}(t)$. The total time dependent perturbation is then the sum of four terms

$$V(t) = V_n(q_i - q_{i-1}(t)) + V_c(\rho_{i-1}(t)) + V_n(q_{i+4}(t) - q_{i+3}) + V_c(\rho_{i+1}(t)). \qquad (16)$$

For the first cluster, the first two terms are replaced by the time-dependent interaction with the impact atom,

$$V_{int}(t) = A \exp[-\alpha(q_1 - q_0(t))]. \qquad (17)$$

5. Semiclassical calculations and analysis

In order to apply the semiclassical formulation, several steps must be followed:

(i) The time-independent cluster eigenvectors $\{\Psi_i\}$ and eigenvalues $\{E_i\}$ are calculated by diagonalizing the cluster Hamiltonian in a direct product basis.

(ii) The time-dependent cluster perturbation $V_1(t)$ is obtained from (16) by integrating the classical equations of motion.

(iii) The close-coupling equations, equation (10), are numerically integrated for specific initial conditions. In these studies, we used $c_1(0) = 1$, $c_i(0) = 0$, $i > 1$, meaning that the cluster starts in the ground state.

The result of these steps is the set of state amplitudes $\{c_i(t)\}$, at a set of discrete times, t_0, $t_1, \ldots t_N$.

The quantum expectation values of the coordinates and mode energies are then calculated:

$$\langle r_k \rangle = \langle \Psi(t) | r_k | \Psi(t) \rangle = \sum_{i,j} c_i^*(t) c_j(t) \langle \Psi_i | r_k | \Psi_j \rangle \qquad (18)$$

$$\langle \varepsilon_k \rangle = \langle \Psi(t) | h_k | \Psi(t) \rangle = \sum_{i,j} c_i^*(t) c_j(t) \langle \Psi_i | h_k | \Psi_j \rangle \qquad (19)$$

where h_k is the Hamiltonian of the Morse oscillator molecule.

The total energy of the cluster is

$$\langle E \rangle = \langle \Psi(t) | H_c^0 | \Psi(t) \rangle + T_{cm} = \sum_{i,j} c_i^*(t) c_j(t) \langle \Psi_i | H_c^0 | \Psi_j \rangle + T_{cm} = \sum_i |c_i(t)|^2 E_i + T_{cm}$$

$$(20)$$

where T_{cm} is the kinetic energy of the centre of mass of the cluster, which is calculated from the classical results.

6. Results and discussion

In the atom–lattice collision studied here, the change in kinetic energy of the impact atom was $\Delta E = (0.376 - 0.140)E_H = 6.41$ eV. The fundamental vibrational spacing for the molecular bond was $\hbar\omega_M = 0.0107E_H = 0.292$ eV. As a result, a total of $\Delta E/\hbar\omega_M = 21.93$ molecular quanta were deposited in the lattice, which amounts to an average of $21.93/20 = 1.097$ quanta per lattice molecule.
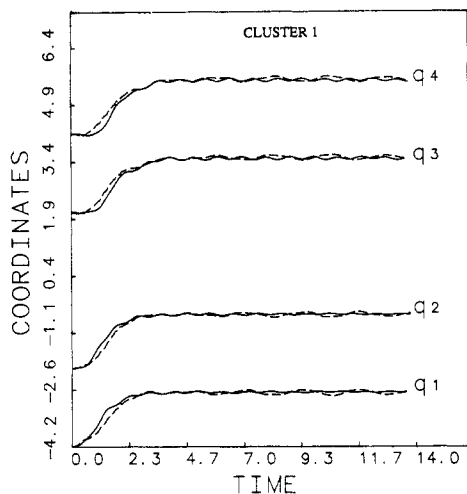
Figure 1. Coordinates of the four atoms in the first cluster. Solid lines are classical results and dashed lines are semiclassical results. Coordinates are in atomic units (a_0) and time is in molecular periods.
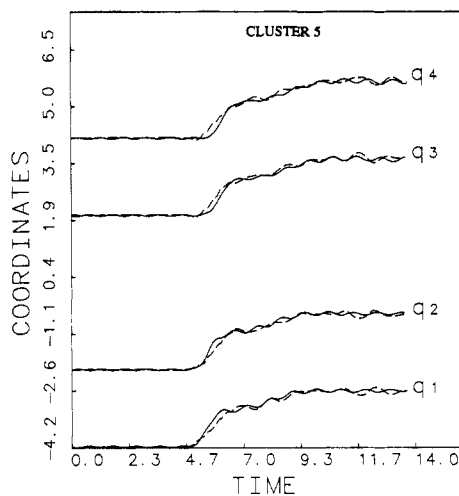
Figure 2. Coordinates of the four atoms in the fifth cluster. Solid lines are classical results and dashed lines are semiclassical results. Coordinates are in atomic units (a_0) and time is in molecular periods.

In equation (15), 360 product basis functions were used, with 6 functions for each of the two molecules, and 10 for the weaker intermolecular bond. Then, the lowest 120 of the cluster eigenfunctions were used in equations (9), (10) for the dynamical evolution. To check for convergence,, the primitive basis size in equation (15) was varied, as was the number of functions N in equations (9), (10). The results shown later in figures 1–5 were not sensitive to these changes. Finally, the Bulirsch–Stoer integrator with Richardson extrapolation was used for the quantum equation, while the variable-step variable-order Adams algorithm was used to solve the classical equations of motion.

In figure 1, both classical and semiclassical coordinates are plotted for the four atoms in the first cluster. The origin is at the centre of mass of the cluster at time $t = 0$. The time is in units of molecular periods, $T = 2\pi/\omega = 0.014\,\mathrm{ps}$, where $\omega = (\beta_M/2\pi)(2D_M/\mu)^{1/2}$. In figure 2, similar results are given for cluster 5. From these two figures, it is apparent that before the shock wave enters the cluster, there is close agreement between the semiclassical and classical results. However, after the shock wave enters the cluster, the agreement is not as close, because of the anharmonicity of the Morse potentials. By comparing the times at which molecules in clusters 1 and 5 are displaced by the shock wave, it is possible to estimate the speed of propagation of the shock wave. This speed is approximately $3.8 \times 10^6\,\mathrm{cm^{-1}\,s}$, which is near the value achieved in various classical simulations: 5×10^5–$1 \times 10^6\,\mathrm{cm^{-1}\,s}$ [14–16], $2 \times 10^6\,\mathrm{cm^{-1}\,s}$ [7], 1.5×10^6–$2.8 \times 10^6\,\mathrm{cm^{-1}\,s}$ [19, 21]. By contrast, the speed of sound in solids at room temperature is usually in the range 0.1×10^6–$0.5 \times 10^6\,\mathrm{cm^{-1}\,s}$.

Previous semiclassical studies of shock wave propagation in a purely harmonic lattice showed excellent agreement with the classical results at all times [28]. This is in accord with Ehrenfest's theorem, which states that the time evolution of quantum expectation valves is isomorphic to the corresponding classical results for harmonic potentials.

Figure 3 shows the total energy for each of the first nine clusters from the classical dynamics calculations. Figure 4 shows the analogous quantity for the semiclassical
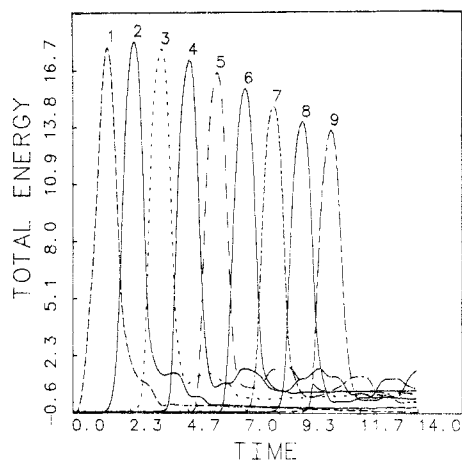
Figure 3. The classical calculated total energies of each cluster. The numbers on the curves identify the clusters. Energies are in units of molecular quanta and time is in molecular periods.
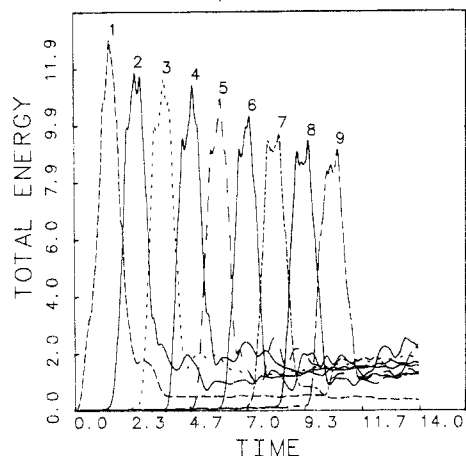
Figure 4. The semiclassical calculated total energy of each cluster. The numbers on the curves identify the clusters. Energies are in units of molecular quanta and time is in molecular periods.
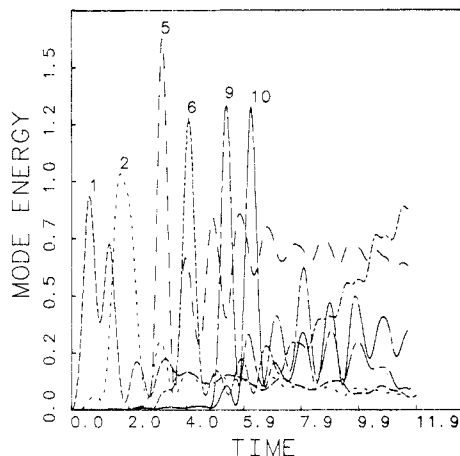
Figure 5. The semiclassical calculated molecular mode energies for the first, third and fifth clusters. The numbers on the curves identify the diatomic molecules. Energies are in units of molecular quanta and time is in molecular periods.

calculations. All energies in these figures are excitation energies in units of molecular quanta, relative to the ground state energy, $(\langle E(t) \rangle - E_{ground})\hbar\omega_M$. Qualitatively, the results are similar, although classical mechanics predicts energies 25–30% higher than the semiclassical calculations.

In both sets of calculations, we observe very clearly the propagation of the shock wave from cluster to cluster, with some energy retained by each cluster, at least during the 12-period time scale shown in the figures.

Figure 5 shows the energy in each molecule (again relative to the ground state) for the first, third, and fifth clusters. Note that each molecule received about one vibrational quantum in less than one vibrational period. The rate of energy transfer is thus 0.292 eV/

0.014 ps = 21 eV/ps. The sum of the energies of the two molecules in each cluster is considerably less than the total energy of each cluster (figure 4); the 'excess' energy goes into molecular relative motion and centre-of-mass motion.

A shock wave launched on one side of the lattice may spall a group of atoms off the opposite side [4]. This effect was observed under the conditions of this study.

From these classical and semiclassical calculations, we obtain the following conclusions about shock wave propagation in a linear molecular lattice with Morse interaction potentials. Because the shock wave is initiated when the ballistic particle strikes the end atom of cluster number one, energy is initially transferred only to the first molecule. However, the bond in this molecule is relatively strong, so the molecule tends to move as a unit, acquiring translational energy as it begins to push the second molecule in the same cluster. Some energy is partitioned into relative motion between these two molecules, some goes into the translational energy of the centre of mass of the cluster and the remainder excites internal motions of the second molecule. Continuing in this way, the energy will transfer from cluster to cluster. For a weak shock wave, anharmonic effects are small and classical mechanics is a good approximation [28]. However, for stronger shock waves, anharmonic effects cause differences between the classical and semiclassical results.

The cluster model as formulated here cannot be used to describe dissociation of molecules within the cluster. However, we are presently extending the model to allow for this case. In addition, it will be possible to do classical calculations on three-dimensional anharmonic lattices, followed by semiclassical calculations on a few impoprtant clusters.

Acknowledgments

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