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On determining the thermal state of individual atoms in molecular dynamics simulations of nonequilibrium processes in solids

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ABSTRACT

An ensemble average approach is proposed for determining the temperature and thermal equilibrium state of individual atoms in solids modeled using nonequilibrium molecular dynamics simulations (NEMD). The basic assumption of the approach is that the atomic velocity of an atom is the sum of a mean mechanical velocity and a random thermal velocity, which can be separated by performing ensemble average of many realizations of the same ensemble. Mechanical and thermal energy field obtained from the decomposed thermal and mechanical velocity together with the thermal velocity distribution reveal the details of energy transfer in these nonequilibrium processes.

1. Introduction

Nonequilibrium thermomechanical processes are ubiquitous and crucial to many areas of studies in science and engineering. Some of the well-known nonequilibrium processes include shock and explosive impacts [1–11], dislocation dynamics [12–14], and cavitation of bubbles [15,16], and the most interesting chemical physics lies in the neighborhood in which deformation is highly localized and temperature is high. For example, the decomposition of shocked energetic materials is usually initiated by a few chemical bonds broken by the shock wave, which may eventually lead to distinct macroscopic processes [1–8]. It has been demonstrated experimentally that after the shock front has passed, the local vibrational and rotational 'quasitemperatures' equilibrate with the translational temperature after a few hundred or thousand vibrational collisions in molecular gas system, where quasistemperature is an effective temperature because temperature is not well defined in the classical statistical mechanics sense when the atoms under consideration are in local thermal nonequilibrium [17]. Reactions at the shock front induced by shock impulses occur at a state far from equilibrium and bond breaking related structural changes happen on a few ps time scale depending on the velocity of shock wave front. It was concluded that the rates of chemical reactions mainly depend on the vibrational quasitemperature.

The atomistic details of many of the nonequilibrium processes can now be studied explicitly using molecular dynamics (MD) simulations with sufficient efficiency and accuracy. Equilibrium MD simulations have been employed to study the thermal decomposition of energetic materials, which enables the characterization of the decomposition processes [18]. Nonequilibrium molecular dynamics (NEMD) simulations, on the other hand, enable the investigation of the atomistic details of detonation waves and have been used to study the role of defects on initiation, the existence of a failure diameter, desensitization, and so forth. For example, NEMD simulations of initial chemical events in RDX (1,3,5-trinitro-1,3,5-triazine) under shock loading were performed and revealed a bimodal response [19]. However, a computational approach based on MD simulations is still lacking which is able to determine accurately the thermal state of individual atoms of a solid undergoing nonequilibrium process. Here the thermal state of an atom refers to whether the atom is in local equilibrium or nonequilibrium and what temperature the atom has at a certain time instant. The development of such method will further elucidate the fundamental relationship between the local thermal state and the chemical kinetics of the process.

In this Letter, we present an 'ensemble average' approach that can determine accurately the thermal state of individual atoms modeled by NEMD simulations. The approach is proposed based on an additive thermomechanical model of the atomic velocity, which is assumed to be the sum of the probabilistic thermal velocity and the deterministic mechanical velocity. It will be demonstrated through the nonequilibrium simulations of shock loading and edge dislocation glide that the approach can be employed to determine the time scale at which an atom stays in nonequilibrium after it is perturbed away from local equilibrium and to analyze the thermal and mechanical energy transfer at the nanoscale.

2. Ensemble average approach

The proposed approach calls for many realizations of the same ensemble of atoms simulated using molecular dynamics (MD) be

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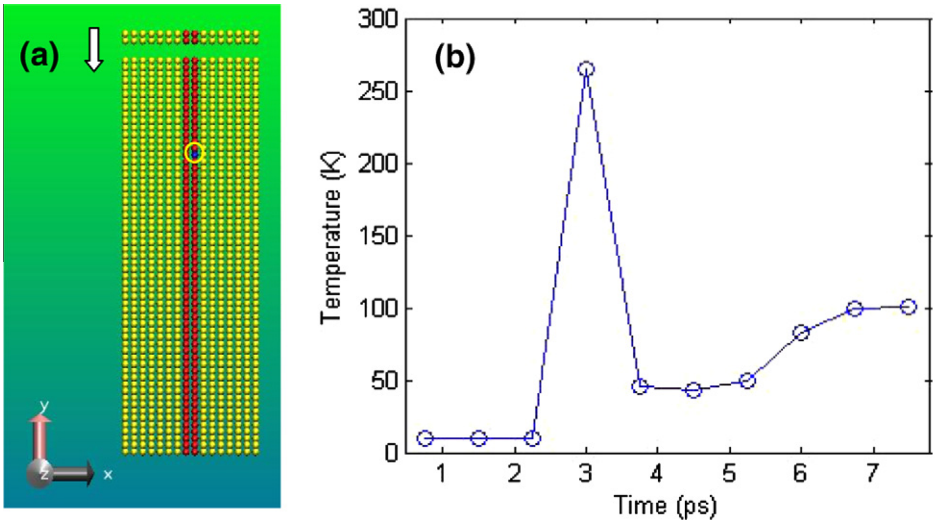

Figure 1. (a) A nickel (Ni) crystal plate subjected to shock loading from the dropping Ni hammer on top (b) transient temperature plot for the selected atom circled in Figure 1(a).

performed so that the atomic velocities from many MD realizations can be gathered and further analyzed to obtain the thermal state of individual atoms. The basic assumption of the approach is that the atomic velocity can be decomposed additively into a mean velocity $\bar{v}$ and a random velocity $\tilde{v}$ at time t:

$$v_\alpha(t) = \bar{v}(x_\alpha, t) + \tilde{v}_\alpha(t), \tag{1}$$

where x_α denotes the position at which the αth atom occupies while the molecular system is in its (possibly local) ground state. The mean velocity $\bar{v}$ will be called the mechanical velocity and the random velocity $\tilde{v}$ will be called the thermal velocity. As will be seen, these denotations elucidate the respective relationship of the velocity fields to the mechanical deformation and heat transfer in the solid the atoms compose. The utilization of the additive model in Eq. (1) can be justified by the fact that it was also employed in the past in the derivation of the hydrodynamics equations of dilute gas via the Boltzmann transport equation [20]. Based on this model, the mean mechanical velocity can be obtained by averaging the obtained atomic velocities over N realizations of the same process simulated using MD simulations, where each realization is initialized by different atomic velocities that conform to the same initial temperature of the system:

$$\bar{v}_{\alpha,i} = \frac{1}{N}\sum_{n=1}^{N} v_{\alpha,i}[n], i = x, y, z \tag{2}$$

where i denotes the direction in the Cartesian coordinate system. The thermal velocity of the nth realization is then obtained through Eq. (1) and (2) by subtracting the resulting mechanical velocity from the atomic velocity.

The thermal velocity data obtained for the N realizations will be employed for determining (1) whether an atom is in local thermal equilibrium or not, and (2) the temperature of an atom. According to statistical mechanics, when an atom is in local thermal equilibrium, its thermal velocity follows the Maxwell–Boltzmann (Gaussian) distribution. Hence, if the random thermal velocity data for an atom obtained from N realizations deviates from the Gaussian distribution, the atom is in nonequilibrium. On the other hand, the temperature of an atom is related to its thermal velocity through the Maxwell–Boltzmann distribution when the atom is in local equilibrium [21–23]. When the atom is in nonequilibrium as manifested by its thermal velocity deviating from the Maxwell–Boltzmann distribution, its temperature is no longer well defined. Dlott [17,24,25] and Chen [23,26] called the temperature measured based on the Maxwell–Boltzmann distribution even when the atom is in nonequilibrium as the quasitemperature or effective temperature. Their idea is adopted in our work and hence the quasitemperature of an atom is computed by:

$$\tilde{T}_{\alpha,i} = \frac{1}{Nk_B}\sum_{n=1}^{N} m|\tilde{v}_{\alpha,i}[n]|^2, \quad i = x, y, z \tag{3}$$

where k_B is the Boltzmann constant. Note that the quasitemperature is a vector quantity instead of a scalar quantity as the quasitemperature has been shown to differ in different directions when the atom is in nonequilibrium. In the rest of the Letter, this will just be called temperature. In turn, the mechanical energy will be computed from the mechanical velocity and expressed in units of temperature:

$$\bar{T}_{\alpha,i} = \frac{1}{k_B} m|\bar{v}_{\alpha,i}|^2, \quad i = x, y, z \tag{4}$$

In this manner, the transport behavior of thermal and mechanical energy can be compared quantitatively in the examples to be presented below.

3. Results and discussions

In the following, the proposed ensemble average approach is applied to two nonequilibrium processes simulated using MD simulations. The thermal state of individual atoms and the interaction between thermal and mechanical energy during each process will be determined and discussed.

3.1. Shock wave propagation

A nickel (Ni) plate is created and modeled by the embedded atom method (EAM) interatomic potential [27,28]. The rectangular domain of the crystal has dimensions of $L_x = 16[1\,0\,0]/2$, $L_y = 32[0\,1\,1]$, and $L_z = 2.8\,[0\,\bar{1}\,1]$ in the x, y, and z direction. Periodic boundary conditions are used in the x and z directions while free surface conditions are employed in the y direction. An impact loading is applied on top of the plate by a smaller Ni plate that has an initial constant velocity of 6 Å/ps in the $-y$ direction (Figure 1a), resulting in a shock wave propagating in the Ni plate. A total of 1000 MD realizations are carried out by varying the initial atomic