Advanced Boundary Conditions for the Simulations of Laser Ablation

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Abstract Irradiating materials with ultra-short laser pulses generates unwanted shock waves which distort the interesting physics. Advanced boundary conditions are presented to erase even very strong shock waves. Depending on the wave length, laser light which leads to ablation may penetrate very deep into the sample. Connection conditions are presented to consistently couple atomistics and continuum description of the sample even at high temperatures together with a discussion of the temperature definition.

1 Introduction

This report will deal with some very important aspects of the atomistic molecular dynamics (MD) simulations of laser ablation coupled with the so-called two-temperature-model (TTM) for the continuum treatment of electrons. Details of the two model parts have been given in a previous HLRS report[14] and by Schaefer and Urbassek [15] for example, and will not be repeated here due to the lack of space. Meanwhile, the physical MD+TTM model has been improved considerably for metals in the thesis of Eisfeld [3] and for covalent materials in the work of Klein [9].

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Even on the biggest available supercomputers atomistic computer simulations are limited to a few micrometers due to the storage requirements of all the atoms and to a few microseconds due to the integration steps of femtoseconds if a typical maximum of a million of steps is assumed.

There are three aspects which can improve the yield of large scale computing considerably: let the first improvement be a better (physical) model and the second a better implementation. Then the third aspect is the reduction of the simulated sample size by special boundary conditions which account for long-range effects. In the case of laser ablation the problem has actually two facets: first of all, shock and tension waves are generated which lead to unwanted effects influencing the ablation process. More generally these processes are directed energy transmissions which do not play a role in macroscopic experiments since there they die out, but are reflected at boundaries in atomistic simulations and pile up, thereby disrupting the simulation sample for example. The second facet is the deep penetration of light into material which requires long samples to simulate time evolution. As the original two-temperature model was formulated as a continuum model not only for the electrons but for the atoms also, it is self-evident to switch back to this model deep in the sample. What is required, are connection conditions between the atomistic part and the continuum part. The paper is organized as follows. After a short digest of heat absorbing boundary conditions for completeness, pressure absorbing boundary conditions are introduced to solve the shock wave problem. Then the spatial coupling of the atomistic part with the continuum description is described together with a discussion of the temperature definition which is necessary for a consistent cooperation of both parts.

2 Heat absorbing boundary conditions

In atomistic materials science simulations samples are often heavily deformed such that they show phase transformations, or cracks are generated for example. The consequence are breaking bonds releasing energy at the crack surface. The sample heats up and uncontrollable melting of the whole sample occurs. In macroscopic experiments this is not a problem since the samples are large enough such that the heat can be compensated. Cracks emit dispersive heat waves which can easily be absorbed by a so-called “stadium” surrounding the crack \[6\]. Since the heat is spread in all directions, the methods work quite well and are well established. In one approach the equations of motion outside the stadium are supplemented with a friction term which removes the heat. In another approach a NVE ensemble which conserves energy is simulated within the stadium and a NVT ensemble is implemented outside the stadium effectively cooling the sample to the desired temperature and thus removing the released energy.
3 Pressure absorbing boundary conditions

An important problem which has to be addressed, regarding the economical simulation of laser ablation is the reflection of shock waves. Such shock waves move at the speed of sound and beyond through the sample and are reflected at the rear surface of the sample. As soon as the reflected wave reaches the original sample surface again it may influence the ablation process considerably, distort the behavior and change the results. In general, this can be avoided by simulating samples long enough, such that the reflected wave arrives at the original surface only when the ablation process has already completed. Therefore, a considerable fraction of processing power and memory is wasted only to compensate for this undesirable effect. This can be avoided by applying pressure absorbing boundary conditions.

A linear or quadratically increasing “damping ramp” [17, 16] which extracts gradually the kinetic energy of the atoms represents a big improvement already. In this case however, the extent of the damping ramp can not be chosen arbitrarily short. The friction term may only increase very slowly otherwise an artificial impedance between neighbouring regions is introduced, resulting again in a reflection. Moreover, an energy ramp also represents a considerable heat sink which, in case of a minimally chosen ramp length may unnaturally increase the heat conduction within the heat-affected zone by amplifying the temperature gradient.

The supposedly most efficient technique for absorption of sound and shock waves in atomistic simulations is based on the so-called “time-history-kernel” method[12, 13, 7]. In this method the equations of motion of the atoms at the free surface are modified as if they were surrounded by neighboring atoms from all sides. The major drawback of this method lies in the fact that it requires the forces of all neighboring atoms for all previous time steps to be present in the current memory, since the modification of the equations of motion rests on a convolution of the atomic trajectories. A considerable simplification is provided by Schaefer and Urbassek[15]. They also modify the equations of motion of the boundary atoms, however, only one restoring force depending on the momenta of the boundary atoms and their center of mass drift velocity is added to the original forces. The latter method has been tested elaborately, however, the success of this method, as mentioned in the publication could be reproduced only for relatively weak shock waves.

A considerable improvement is provided by the absorbing boundary conditions according to Ming and Fang[11, 4]. By additionally considering the momenta and positions of the next neighbors the authors formulated on the basis of a simple spring-sphere model with linearized forces a highly efficient solution to the problem. Furthermore they abstained from the simplification of the shock wave as a scalar wave and treated the involved atomistic displacements in a complete vector wave picture. In our test simulations, their modified equations of motion for the boundary atoms withstood shock waves with intensities up to 40 GPa and beyond, as long as the material in close
proximity to the free surface did not lose its original crystallinity due to phase transitions or plastic deformation.

A more elaborate description of the model with appropriate derivations may be found in the original publications. Here we restrict ourselves to the formulation of the modified equations of motion for the boundary atoms in a (100)-oriented face centered cubic crystal (fcc). The positions of the atoms are given by the indices \(l, m, n \in \mathbb{Z}_0\) of the lattice sites. For the boundary atoms, namely the atoms belonging to the lattice plane at the free surface, \(l = 0\). For the neighboring atoms a lattice plane deeper into the crystal \(l = 1\).

The displacement \(u_{0,m,n}\) of a boundary atom from its original equilibrium position follows the equation of motion

\[
\dot{u}_{0,m,n} = \sqrt{\frac{k}{M}} u_{0,m,n} \cdot \begin{pmatrix}
1 & 0 & 0 \\
0 & -2\sqrt{2} & 0 \\
0 & 0 & -2\sqrt{2}
\end{pmatrix} + \sqrt{\frac{k}{M}} u_{0,m,n} \cdot \begin{pmatrix}
1 & 0 & 0 \\
0 & \sqrt{2}/2 & 0 \\
0 & 0 & \sqrt{2}/2
\end{pmatrix} \left( u_{1,m+1,n} + u_{1,m-1,n} + u_{1,m+1,n} + u_{1,m-1,n} \right)
-
\frac{1}{4} \left( \dot{u}_{1,m+1,n} + \dot{u}_{1,m-1,n} + \dot{u}_{1,m+1,n} + \dot{u}_{1,m-1,n} \right),
\]

where \(k\) is the force constant and \(M\) the mass of the atom according to the sphere-spring model. Thus, only the four nearest neighbors in the lattice plane \(l = 1\) have to be taken into account. This situation is represented in Fig. 1.

The force constant can be computed from the potential analogously to the elaboration of Schaefer and Urbassek. Alternatively, it can be fitted to the particular intensities of the shock waves in a series of test simulations. The latter procedure is more tedious, but in the end leads to better results since here, effects which go beyond the strongly simplified sphere-spring model can also be compensated for.

For our model material aluminum, satisfactory results could be achieved with \(k = 0.9 \text{eV/Å}^2\). The efficiency of the method can be seen in the contour plots for the temporal evolution of the hydrostatic pressure. The sample surface in this quite extreme example is heated during the first 300 fs so strongly, that the generated shock wave hits the rear side of the sample, which is only a few nanometers apart from the original surface with an intensity of about 25 GPa. Without pressure absorbing boundary conditions the wave is reflected at the rear side and its sign is flipped, giving rise to an intensity of 5 GPa. As a consequence, the rear side of the sample bursts into numerous fragments, a mechanism commonly referred to as spallation. In addition, the reflected wave reaches the front surface shortly thereafter. The application of the pressure absorbing boundary conditions on the contrary only leads to

\[1\] Where the crystallographic (1, 0, 0)\(^T\)-direction is parallel to the simulation box axis \(x\).
a temporary buckling at the rear side of the sample. The crystal structure remains intact and spallation is suppressed. Certainly, the reflection in this extreme case cannot be avoided completely but there is no doubt that the intensity of the wave is largely reduced.

The inspection of the atomistic snap shots in 3 shows the differences even more clearly. The wave at the rear side of the sample is gradually absorbed and after 10 ps the sample is already nearly completely stress-free except for the heat affected zone (left). Without the modified equations of motion it cannot be avoided that, disregarding the spallation, the stresses of the reflected wave further drive the ablation process of the material at the surface. Moreover, the passage of the reflected stress wave gives rise to numerous stress-nuclei even below the heat affected zone.

4 Coupling to the TTM

The pressure absorbing boundary conditions involved only the atomistic part of the problem. In the combined MD+TTM model light might penetrate several micrometers deep into the sample and heat up the sample. This would again require very long samples which effectively represent a waste of resources since nothing of interest is going on so deep into the sample. Replacing atomistics by a finite-difference description can solve this problem.
Fig. 2: Histogram plot of the temporal pressure-evolution after sudden heating of the surface of a (100)-oriented aluminum single crystal. (a) represents the situation with pressure absorbing boundary conditions, whereas (b) demonstrates what happens without these modified equations of motion. Along the x-axis the position below the original surface $x = 0$ is displayed.

5 Implementation of the two temperature model

The numerical treatment of the energy balance equation is non-trivial and thus should be considered in some detail. The source term of the irradiated laser energy and coupling term to the molecular dynamics simulations will not be considered since they are irrelevant for the description of the essential numerics. The balance equation for the internal, specific energy of the electronic subsystem $e$ (internal energy per mass of the corresponding material), involving only drift and diffusion may be formulated as

$$ \frac{\partial (\rho e)}{\partial t} = \nabla \cdot (\kappa_e \nabla T_e) - \nabla \cdot (\rho u e), $$

(2)

where $\kappa_e$ corresponds to the electronic heat conductivity, $T_e$ is the electronic temperature, $\rho$ represents the material density, and $u$ is the drift velocity.

The first step to solve equation 2 is to chose a suitable discretization of the simulation domain. Since molecular dynamics are combined with a hy-
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Fig. 3: Molecular dynamics snap shots of the hydrostatic stress after passage of shock and tension waves after sudden heating of the material surface at $x = 0$. On the left side, the situation with pressure absorbing boundary conditions is displayed and the right side represents the situation without any modifications of the original equations of motion. The absorption of the pressure wave at the rear side of the sample can be seen clearly in the left part of the figure. The crystal structure is conserved despite the temporary buckling at the end of the sample. The same shock wave leads to spallation at the read side of the sample without pressure absorbing boundary conditions. In addition, the reflected stress wave soon reaches the heat affected zone where it leads to an enlargement of the distorted region. Furthermore, several stress-nuclei are left behind, even below the heat affected zone. Along the directions perpendicular to the beam direction, periodic boundary conditions have been applied.

droodynamical description of the electronic subsystem in the present hybrid approach, it is favorable to use the MD domain decomposition of the sample into partial volumes also for the hydrodynamics part. Zhigilei and Ivanov[18] described how every MD-cell or typically a group of such cells can be interpreted as a node of a finite-difference (FD) grid. The volume of the FD node corresponds to the combined volumes of the participating MD-cells.

Typical beam diameters in experiments are in the range of a few microns. For metallic samples they are thus far larger than the optical penetration depth of light which lies in the range of $10^{-20}$ nm. For this reason it is sufficient to model the laser-metal interaction in a one-dimensional approximation. By neglecting the transverse beam profile, the surface of the sample
is heated homogeneously by the laser. The resulting temperature gradient thus exhibits, to a good approximation only a component parallel to the optical beam axis. The perpendicular components are negligibly small, even if the material is not isotropic. This permits to apply periodic boundary conditions along these transverse directions. In the end a tiny volume element of the sample in the center of the beam is considered. This situation is displayed in Fig. 4. To further reduce the computational load, an additional FD-lattice is attached at the end of the MD-simulation domain, where the original two-temperature model is treated only on the continuum level. The MD-simulation domain is thus limited to the interesting part of the sample where the material is ablated, melts, dislocations and other material restructuring processes occur. The task of the “virtual” FD-lattice only consists in providing a natural heat flux of the electronic subsystem. Otherwise heat might build up at the rear side of the sample and tamper the temperature gradient. Within the virtual lattice, heat diffusion is limited to the electronic subsystem only. The relatively slow heat diffusion of the lattice is neglected. The equation of state according to Levashov [10] yields for the heat capacity of the lattice at 300 K a value of $8.59 \cdot 10^2 \text{JK}^{-1}\text{kg}^{-1}$. The pressure absorbing boundary conditions are located between the two simulation domains as shown in4. The modification of the equations of motion as they are exemplified in 3 not only lead to the absorption of elastic waves but reduce also the kinetic energy of the atoms and thus the temperature at the rear side of the sample. For this reason, the virtual lattice does not couple directly to the end of the sample, but contrary to the situation shown in figure, few atomic layers further down into the crystal lattice, where the lattice is not affected by the cooling effect of the boundary conditions. The region in between serves as a thermal buffer only.

An important question which has to be addressed first is how large such a FD-cell has to be. The question is in principle equivalent to the question if a scale separation exists between the collision-mediated relaxation to the local equilibrium and the diffusion-determined relaxation to the global equilibrium which permits a continuum treatment of the particle collective. A detailed treatment of the problem can be found in [3]. Here we will only summarize the results.

The mean square displacement of a particle $l^2$ has to be much larger than the mean-free path between two collisions $\lambda_{\text{mfp}}$. The continuum description of the electron collective is indeed valid if

$$l \gg \lambda_{\text{mfp}}.$$ (3)

For aluminum the mean thermal velocity can be approximated in a large temperature range by the Fermi-velocity $v_F \approx 1.5 \cdot 10^6 \text{m/s}$. Furthermore the effective collision frequency is equal to $\Gamma_{\text{eff}} \approx 8.5 \cdot 10^{14}/\text{s}$ [2] at room temperature already, such that the lower limit of the mean free path $\lambda_{\text{mfp}} \approx 1.2 \text{fs} \cdot 2 \cdot 10^6 \text{m/s} \approx 2.4 \cdot 10^{-9} \text{m}$. A FD cell should therefore possess a
Fig. 4: Schematic illustration of the hybrid MD/TTM ansatz. The simulation focuses on a small volume element of the whole sample, which is located in the very center of the laser beam. The lateral beam profile can be neglected in this one-dimensional approximation. The MD part of the model is limited to the heat affected zone to save resources. The MD simulation domain is enlarged by a “virtual” FD-lattice at the end of the sample to guarantee a natural heat flux of the electronic sub-system.

characteristic length of a few nanometers to permit a continuum description of the enclosed electron gas. At a temperature of $T = T_i = T_e = 3000$ K for example $\Gamma_{\text{eff.}} \approx 2.6 \cdot 10^{16}$ s$^{-1}$ [5] is obtained and the characteristic length results in $\approx 0.8$ nm only. $T_i$ is the lattice temperature.

As important as the size of the FD cell is the number of the atoms contained inside the cell, since in MD the temperature corresponds to the average kinetic energy of an atom which moves with the most probable velocity $v_{\text{therm.}}$ of the Maxwell-Boltzmann distribution.

In order to be able to define a temperature for an atom collective, first a Maxwell-Boltzmann distribution has to be present and second, the most probable velocity has to be known. The first condition is problematic already since the strong acceleration of the atoms by the heated electrons forces the lattice atoms into a temporal non-equilibrium. This fact can be neglected
if the equilibrium is reached fast enough. Kinetic gas theory again provides a rough estimate based on a simple geometric consideration of two elastically colliding hard spheres. If the deviation from the Maxwell-Boltzmann distribution is small then the relaxation time is calculated with

$\tau_{\text{MB}} = \frac{m^{1/2}}{4\pi^{1/2}d^2(k_B T)^{1/2}n_i}$, \hspace{1cm} (4)

where for aluminum, the mass of the atom $m \approx 4.32 \cdot 10^{-26}$ kg, the particle density at standard conditions $n_i \approx 6.25 \cdot 10^{28}$ m$^{-3}$ and the particle diameter, as well as the average distance resulting from the particle density, respectively, $d \approx 1.56 \cdot 10^{-10}$ m. Thus at $T = 300$ K the relaxation time $\tau_{\text{MB}}(300 \text{K}) \approx 3 \cdot 10^{-13}$ s and at high temperatures, for example $\tau_{\text{MB}}(10000 \text{K}) \approx 3.5 \cdot 10^{-14}$ s. Therefore, for minor deviations from the equilibrium distribution, the actual non-equilibrium may be neglected for increasing temperatures.

The second condition requires the number of atoms within a single FD cell to be big enough, such that the average atomic velocity exhibits a statistical significance. Universally accepted is a number on the order of the Avogadro-constant $\approx 10^{23}$, while some authors refer to a few hundreds of atoms$^1$. In this regard, a thought experiment might be helpful:

From a reservoir of infinitely many particles of type $A$ and $B$ subsequently $N$ particles are drawn. The number of possibilities to draw $N_A$ particles of type $A$ and $N_B$ particles of type $B$ is thus

$\Omega(N_A, N_B) = \frac{N!}{N_A!N_B!} = \frac{N!}{N_A!(N-N_A)!} = \binom{N}{N_A}$, \hspace{1cm} (5)

If the reservoir contains equally many particles of type $A$ and $B$ then the most probable outcome of the experiment is $N_A = N_B = N/2$, where in the limit

$\lim_{N \to \infty} \Omega(N_A, N_B) = \Omega(N/2, N/2) = \frac{N!}{(N/2)!(N/2)!}$. \hspace{1cm} (6)

If the resulting distribution is presented as a function of $N_A/N$ or $N_B/N$ then, with increasing $N$ the distribution converges to a Gaussian centered at 1/2 with a standard deviation $\propto N^{-1/2}$, see Fig. 5.

This simple thought experiment can be generalized to an arbitrary number of particle types which, in a transferred sense, can represent separate energy levels (in the NVE ensemble).

In this case, the $x$-axis corresponds to the energy of the state in consideration $E_i$ and the $y$-axis to the occupation probability $P(E_i) = \Omega(E - E_i)/\sum_j \Omega(E - E_j)$ which would be maximal at the internal energy $U = \langle E \rangle$, where $E$ represents the total energy of the system.

The standard deviation for $N \approx 100$ results in about 3% while for $N \approx 1000$ it falls below 1% as can be seen in Fig. 5(b). This confirms the claim
in [1] that a few hundred atoms lead to a reasonable average of the thermal energy already and thus provide a useful estimation of the temperature.

![Graph](image.png)

**Fig. 5:** Illustration of the relative probability to draw $N_A$ particles of type $A$ out of a reservoir of a total of $N$ equidistributed particles (a) and the corresponding standard deviation (b).

### 6 Conclusion

Two improvements for large-scale computer simulations have been described. In materials science there are many studies of multi-scale simulations coupling atomistic and meso-scale finite-element methods. Sometimes even a further layer is added describing the interaction by ab-initio-methods. These approaches typically work only due to the fact that they are close to equilibrium and no dynamical processes like strong waves occur. Here we have described on how to erase strong waves and how to consistently deal with long-range phenomena avoiding expensive atomistic simulations. The hope is that the ideas presented can also be applied in other circumstances.

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