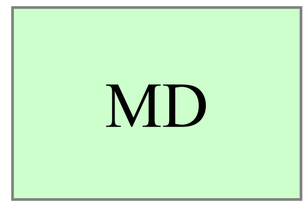
Boundary Conditions

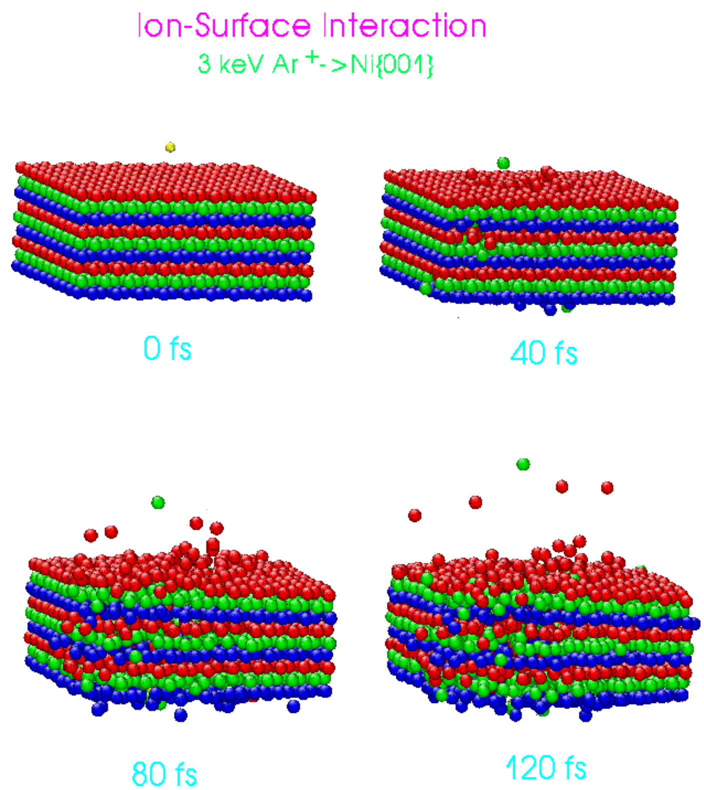
The length-scale of MD is limited – a large fraction of the atoms is on the surface or "feel" the presence of the surface. How to reproduce interaction of atoms in the MD computational cell with the surrounding material?

1. Free boundaries (or no boundaries). This works for a molecule, a cluster or an aerosol particle in vacuum. Free boundary condition can be also appropriate for ultrafast processes when the effect of boundaries is not important due to the short time-scale of the involved processes, e.g. fast ion/atom bombardment, etc.



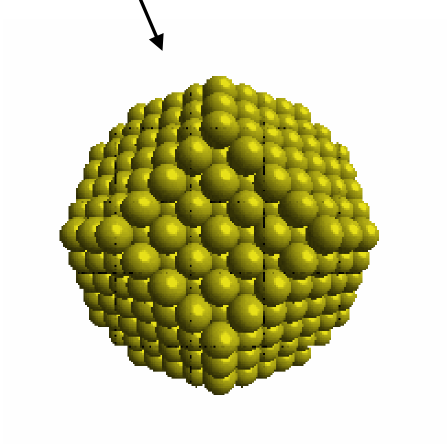
Examples of free boundary conditions in MD:

Ultrafast process of sputtering



keV particle bombardment, by Barbara Garrison
http://galilei.chem.psu.edu/Research_bmb.html

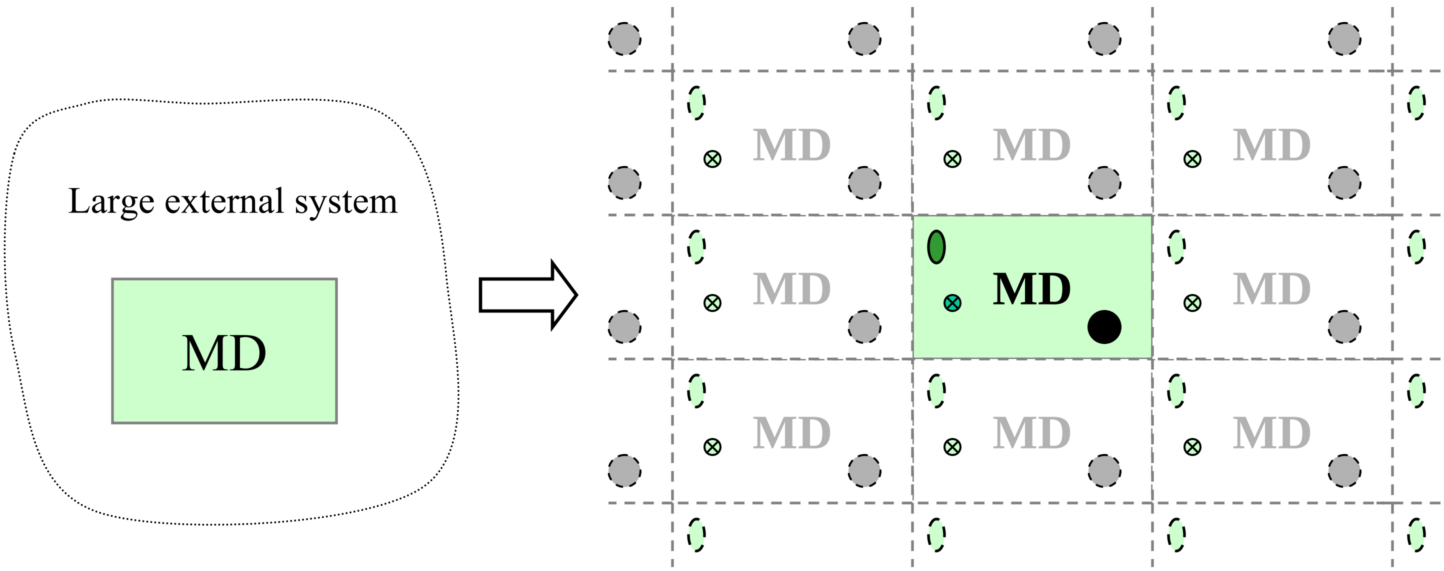
Free cluster



2. Rigid boundaries (atoms at the boundaries are fixed). In most cases the rigid boundaries are unphysical and can introduce artifacts into the simulation results. Sometimes used in combination with other conditions (stochastic and periodic conditions, as discussed below).

Boundary Conditions

3. Periodic boundary condition (eliminates surfaces – the most popular choice of boundary conditions). This boundary conditions are used to simulate processes in a small part of a large system.



All atoms in the computational cell (green box) are replicated throughout the space to form an infinite lattice. Than is, if atoms in the computational cell have positions $\mathbf{r}_i$, the periodic boundary condition also produces mirror images of the atoms at positions defined as

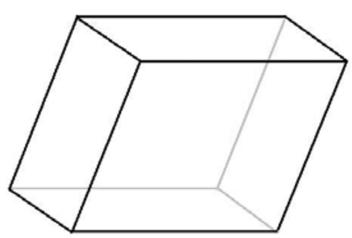
$$\vec{r}_i^{\,image} = \vec{r}_i + l\vec{a} + m\vec{b} + n\vec{c}$$

where **a**, **b**, **c** are vectors that correspond to the edges of the box, l, m, n are any integers from -∞ to +∞.

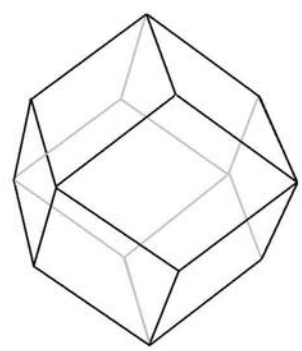
Each particle in the computational cell is interacting not only with other particles in the computational box, but also with their images in the adjacent boxes.

The choice of the position of the original box (computational cell) has no effect on forces or behavior of the system.

Most simulations are done with cubic computational cells, but other shapes, such as truncated octahedral or rhombic dodecahedral cells, are possible. Non-cubic shapes can be used, for example, to eliminate the influence of the cubic symmetry on a shape of a crystal nucleus in a liquid.



parallelepiped MD cell



rhombic dodecahedral MD cell

Boundary Conditions

Limitations of the periodic boundary condition:

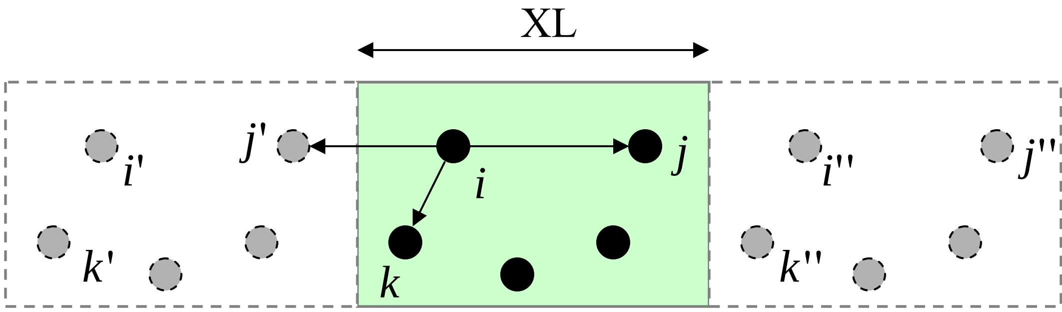
- The size of the computational cell should be larger than $2R_{cut}$, where R_{cut} is the cutoff distance of the interaction potential. In this case any atom i interacts with only one image of any atom j. And it does not interact with its own image. This condition is called “minimum image criterion”.

- The characteristic size of any structural feature in the system of interest or the characteristic length-scale of any important effect should be smaller than the size of the computational cell.

For example, low-frequency parts of the phonon spectrum can be affected, stress fields of different images of the same dislocation can interact, etc. To check if there are any artifacts due to the size of the computational cell – perform simulations with different sizes and check if the result converges.

Calculation of distances between atoms with periodic boundary conditions:

When the minimum image criterion is satisfied, a particle can interact only with the closest image of any other particle.



The closest image may or may not belong to the computational cell. Therefore, in the code, if a particle j is beyond the range of interaction with particle i ($R_{ij} > R_{cut}$), we have to check the closest images. For example, in MSE627-MD code, an algorithm for checking the closest image is:

```
IF(LIDX.EQ.1) THEN
   IF(DX.GT.XLHALF) DX=DX-XL
   IF(DX.LT.-XLHALF) DX=DX+XL
ENDIF
```

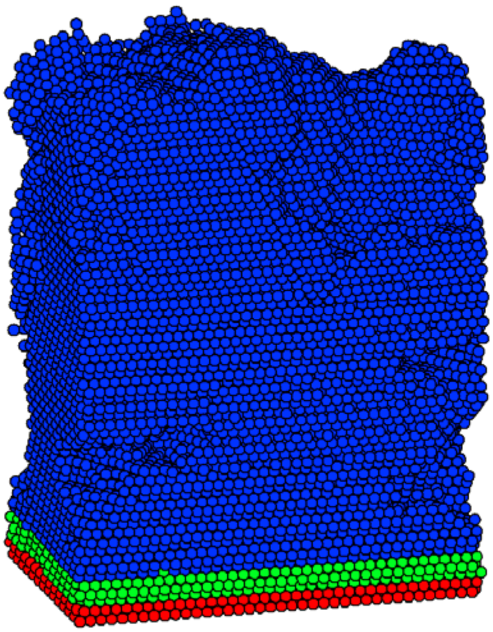
where $DX = X_j - X_i$,

$XLHALF = XL/2$

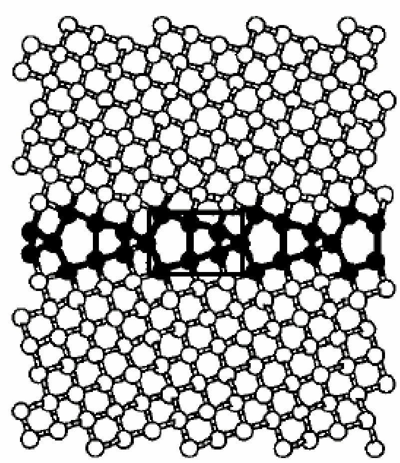
Boundary Conditions

4. **Mixed boundary conditions -** periodic in one/two directions, free/rigid in other.

In order to apply periodic boundary conditions in all directions the system should be isotropic or periodic. This is not always the case. For example, if we study a grain boundary, we may have periodicity in the directions parallel to the grain boundary, but not in the perpendicular direction. Dislocations break periodicity and do not allow for use of the periodic boundaries.



Cluster deposition film growth, by Dongare et al. Periodic boundary conditions in the directions parallel to the substrate, rigid and constant T layers at the bottom.



Grain boundary (GB) in diamond

by Shenderova et al.

Periodic boundary conditions in the directions parallel to the GB plane, free hydrogen-terminated in the direction perpendicular to the GB.

In many cases more complex, damping/non-reflecting/stochastic boundaries and boundary regions, combined MD-FEM approach, etc. are needed, as discussed below.

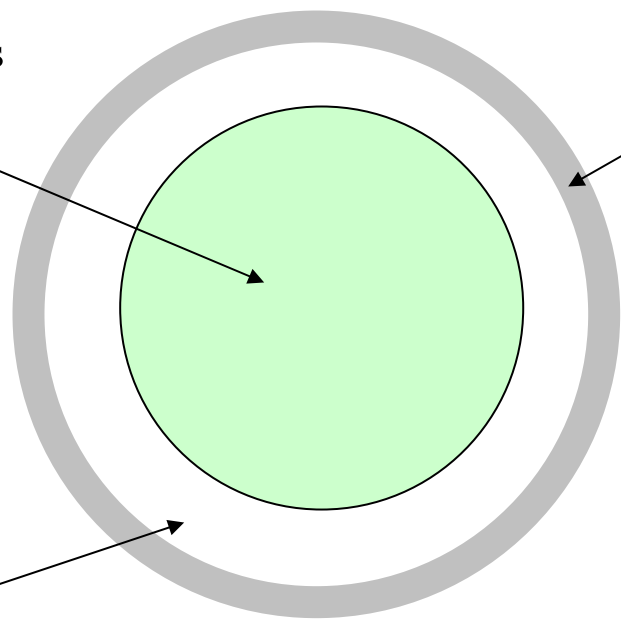
Thermal conduction, $\tau_{th} \sim L^2/D_T$. For organic solids $D_T \approx 10^{-7}$ m²/sec, and for 50 nm sample $\tau_{th} \sim 25$ ns. → can deal with thermal conduction by brute force approach – just increase size of the MD computational cell.

What about metals? $D_T \approx 10^{-4}$ m²/sec for gold. Thermal conduction is important, especially for simulation of long processes such as film growth, reactions on surfaces etc.

Acoustic wave propagation, $\tau_s \sim L/C_s$ ($C_s \sim 1000$-10000 m/s). For 50 nm sample $\tau_s <$ 50 ps. → always need some special boundary conditions to avoid reflection of an acoustic wave from the bottom of the computational cell.

Stochastic Boundary conditions

Stochastic boundary conditions can be considered as the replacement of atoms beyond a given distance by a thermal bath model. The interaction between the bath and the dynamic region (or "reaction region") should preserve the equilibrium structure and structural fluctuations and should act as a source and sink for the local energy fluctuations in the reaction region.



The description of the stochastic region can be based on the generalized Langevin equation. A special case – the Langevin equation, derived under assumption that the thermal bath retains no memory of what the system did in the past, is often used in MD simulations:

$$m \, dv_i / dt = -m\beta v_i + R_i - \partial U / \partial r_i$$ - Langevin equation

The method is originally developed for simulations of gas-surface reactions by S. A. Adelman and J. D. Doll, *J. Chem. Phys.* **61**, 4242 (1974); *J. Chem. Phys.* **62**, 2518 (1975); *J. Chem. Phys.* **64**, 2375(1976); *J. Chem. Phys.* **63**, 4908 (1975).

It was later adapted in simulations of many other phenomena, e.g. liquid phase reactions in *Chem. Phys. Lett.* **90**, 215, (1982); *J. Chem. Phys.* **79**, 6312, (1983).

Stochastic Boundary conditions

$$m\,{}^{dv_i}\!/_{dt} = -m\beta v_i + R_i - {}^{\partial U}\!/_{\partial r_i}$$ - Langevin equation

- thermal motion of particles is driven by random force
- a friction force and a random force R_i are added to the equation of motion
- the temperature is kept at a constant value by the balance between the thermal agitation due to the random force and the slowing down due to the friction

β – friction coefficient of an atom that, within the Debye model, can be determined from the relation $\beta = 1/6\ \pi\ \omega_D$, where ω_D is the Debye frequency, $\omega_D = k_B\Theta_D/\hbar$, and Θ_D is the Debye T

R_i – random white noise forces with Gaussian distribution centered at zero. The width of the distribution is defined by temperature and should obey the second fluctuation-dissipation theorem [R. Kubo, *Rep. Prog. Theor. Phys.* **33**, 425, 1965]:

$$\left\langle R_i(t) R_i(0) \right\rangle = 2\ kT\ m\ \beta\ \delta(t)$$

The second fluctuation-dissipation theorem takes care of balancing the increase in energy due to the random fluctuating force and the decrease in energy due to the friction force.

$$W(R_i) = \left(2\pi\left\langle R_i^2\right\rangle\right)^{-\frac{1}{2}} \exp\left(\frac{R_i^2}{2\left\langle R_i^2\right\rangle}\right)$$

where <…> denotes average over an equilibrium ensemble and $W(R_i)$ is the probability distribution of the random force.

To implement in MD we have to average over a timestep Δt:

$$R_n = \frac{1}{\Delta t}\int_{t_n}^{t_{n+1}} R(t)\,dt \qquad \left\langle R_n^2\right\rangle = \frac{2kTm\beta}{\Delta t} \qquad \left\langle R_n\right\rangle = 0 \qquad \left\langle R_n\, R_{n+1}\right\rangle = 0$$

R_n is taken from Gaussian random number generator. Methods for generating random numbers with Gaussian distribution from evenly distributed random numbers can be found in [M. Abramovitz, *Handbook of Mathematical Functions*, 9th edition, 1970, p. 952]

The approach described above is used by M. Berkowitz and J.A. McCammon, Chem. Phys. Lett. **90**, 215 (1982). More complex and rigorous descriptions of Langevin particles has been discussed in literature, e.g. J.C. Tully, *J. Chem. Phys.* **73**, 1975 (1980).

Boundary condition for thermal conduction

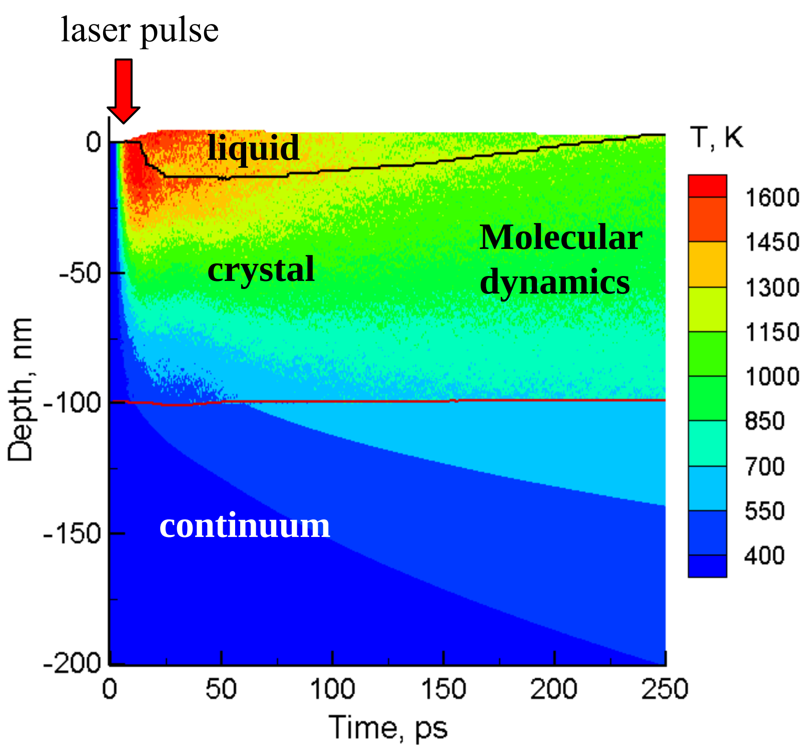
In metals heat flow is dominated by electrons, while in insulators heat is transmitted solely by phonons. The electronic heat conduction is typically much faster than the phononic one..

- In the simulations when a relatively slow phononic heat transport does not lead to the development of a strong temperature gradient within the computational cell, adding a boundary region of constant temperature (e.g. thermal bath discussed above) may be sufficient. This approach is commonly used in simulations.

- Special boundary conditions based on the Fourier's law and implemented by scaling the velocity of atoms in the boundary region can be designed, e.g. [Y. Wu and R. J. Friauf, *J. Appl. Phys.* **65**, 4714, 1989].

- In simulations performed for metals, the evolution of temperature field beyond the MD computational cell is often needed, especially if the processes under study involve deposition or removal of large amounts of energy. In these cases, a combined continuum-atomistic approach can be used, when the electronic energy transport is modeled at the continuum level and in a larger spatial domain.

  For example, a combined continuum-atomistic model has been developed for simulation of laser-induced processes in metal targets [Lin, Johnson, Zhigilei, *Phys. Rev. B* **77**, 214108, 2008]. The model provides a seamless transition of the temperature field from the MD part of the model to the much larger continuum part:



Laser melting and resolidification of a surface region of Ni target irradiated by a 1 ps pulse at an absorbed fluence of 43 mJ/cm^2.

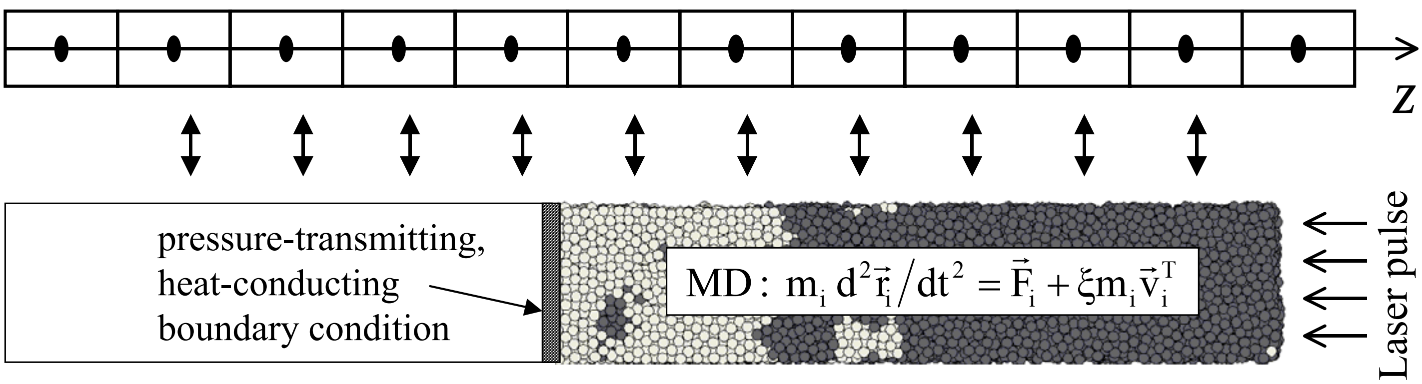
Only part of the continuum part of the model (500 nm total) is shown in this figure.

The model is briefly described in the next page.

Continuum – atomistic model for electronic heat conduction

The electronic energy transport is modeled at the continuum level, by solving the heat conduction equation for the electronic temperature can be solved by a finite difference method and the energy exchange between the lattice and the electrons is described by adding an additional term to the MD equation of motion.

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \frac{\partial}{\partial z}\left(K_e(T_e, T_l)\frac{\partial}{\partial z}T_e\right) - G(T_e - T_l) + S(z, t)$$



$$C_l(T_l)\frac{\partial T_l}{\partial t} = G(T_e - T_l) \qquad T_l^{cell} = \sum_{i=1}^{N^{cell}} m_i \left(\vec{v}_i^T\right)^2 \Big/ \left(3k_B N^{cell}\right)$$

C and K are the heat capacities and thermal conductivities of the electrons and lattice as denoted by subscripts e and l, and G is the electron-phonon coupling constant.

The source term S(z,t) is used to describe the local laser energy deposition per unit area and unit time during the laser pulse duration (conduction band electrons absorb the laser energy).

In the continuum equation for the lattice temperature a term responsible for the phonon heat conduction is omitted since it is typically negligible as compared to the electron heat conduction in metals.

Cells in the finite difference discretization are related to the corresponding volumes in the MD system. The lattice temperature and coefficient ξ are defined for each cell.

The expression for coefficient ξ and the derivation of the coupling term in MD is given in Appendix A of [*Phys. Rev. B* **68**, 064114, 2003].

Note that the electronic heat conduction is not accounted for in the classical MD and the combined approach is needed not only to provide a heat-conducting boundary condition but also to correctly describe the heat conduction inside the MD part of the model.

Continuum – atomistic model for electronic heat conduction

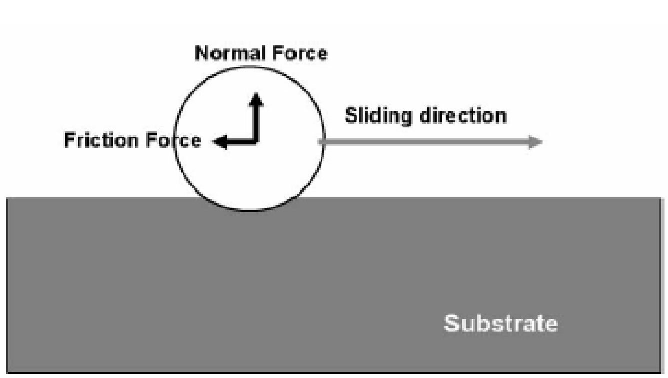
J. D. Schall, C. W. Padgett, and D. W. Brenner, Ad hoc continuum-atomistic thermostat for modeling heat flow in molecular dynamics simulations, *Molecular Simulation* **31**, 283–288, 2005: **simplified continuum-atomistic thermostat scheme.** Applied for frictional heating by a tip sliding along the surface.

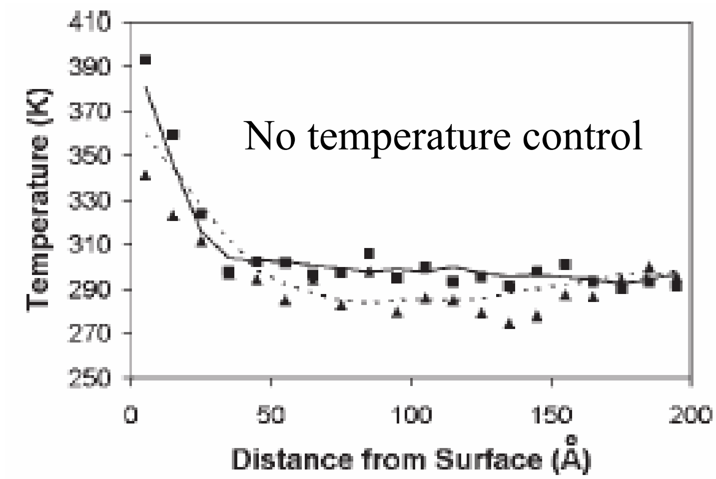
$$\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial z^2}$$

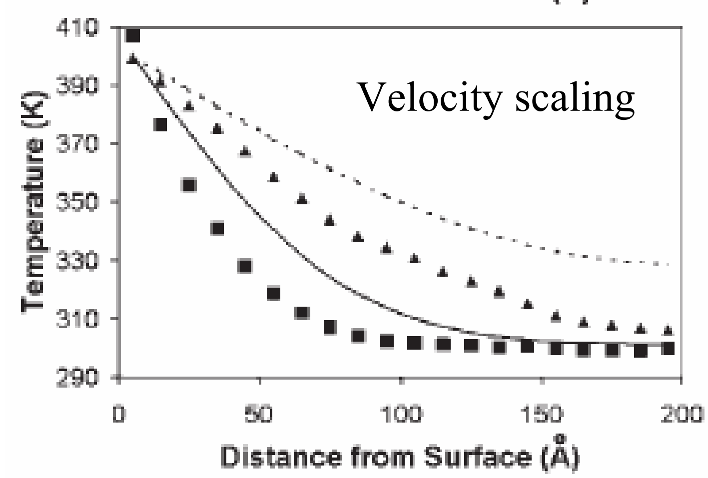
$$T^{new} = T^{old} + \Delta t D\frac{\partial^2 T}{\partial z^2}$$

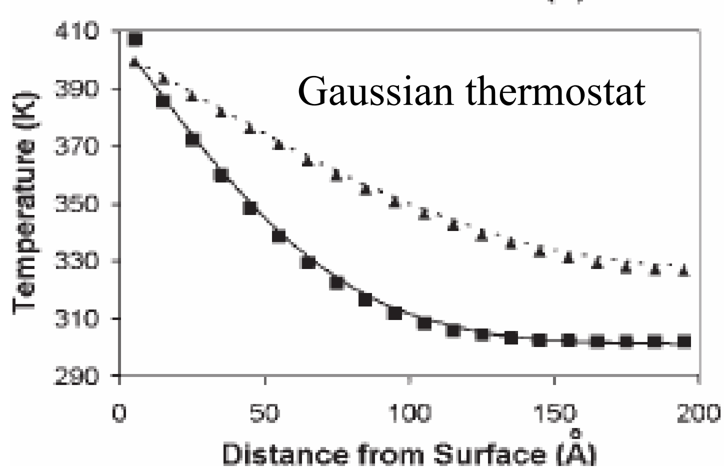
T^{new} is enforces in each cell using the Gaussian thermostat method for constant-temperature simulations Phys. Rev. A 28, 1016, 1983.

The method is applied for frictional heating by a tip sliding along the surface

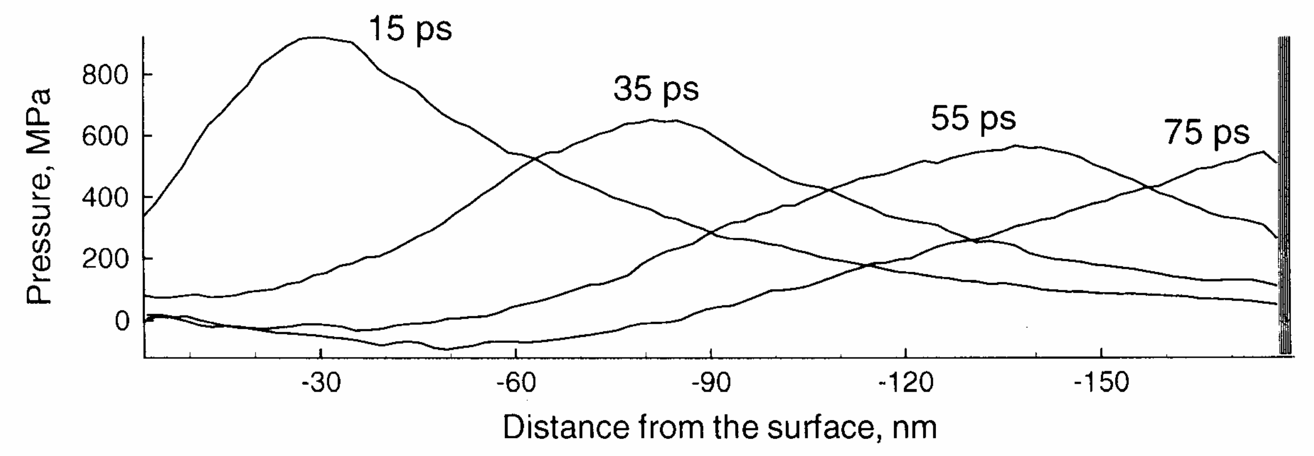




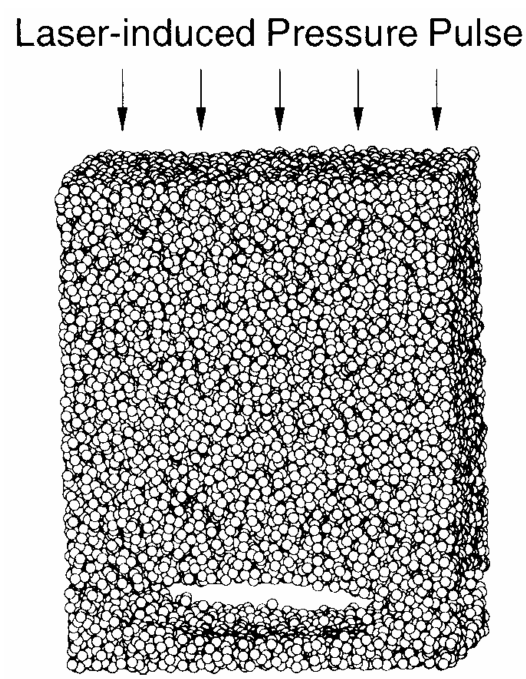




Propagation of Acoustic Waves



Propagation of the pressure wave occurs at the length-scale that is beyond the capability of MD simulation



Rigid Boundary

Rigid and free boundary conditions lead to the reflection of the pressure wave and can cause back spallation

Acoustic emissions in the fracture simulation in 2D model

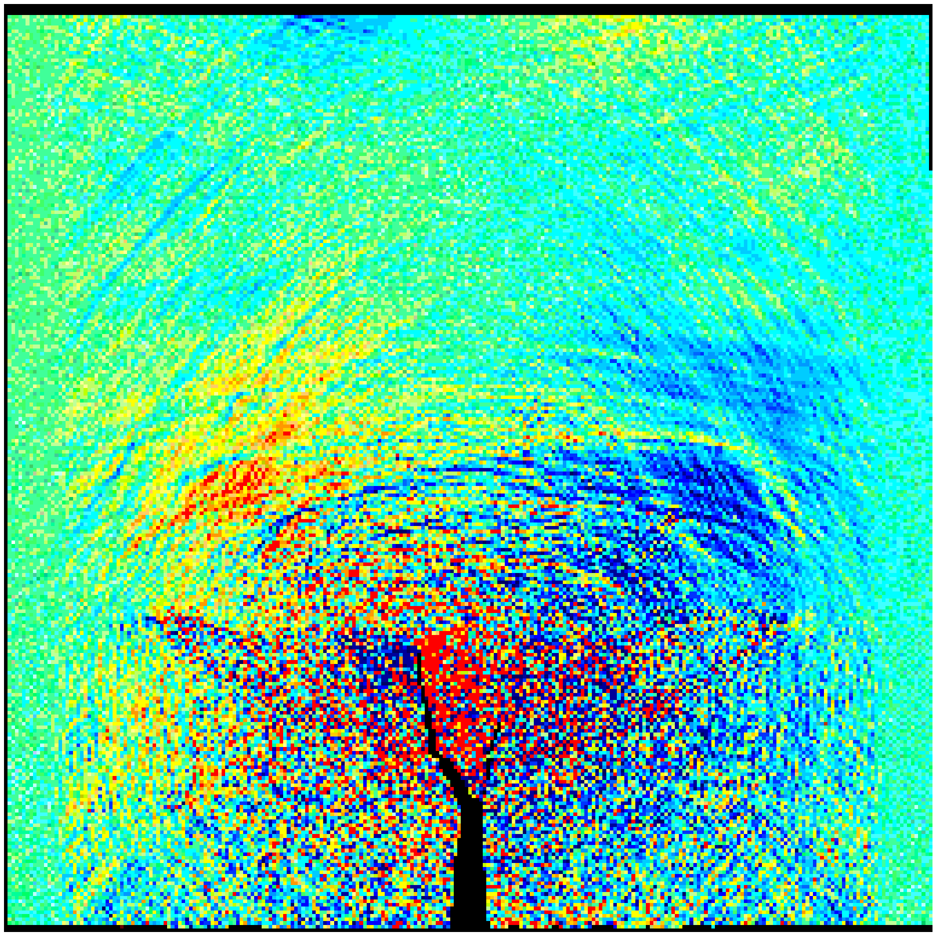
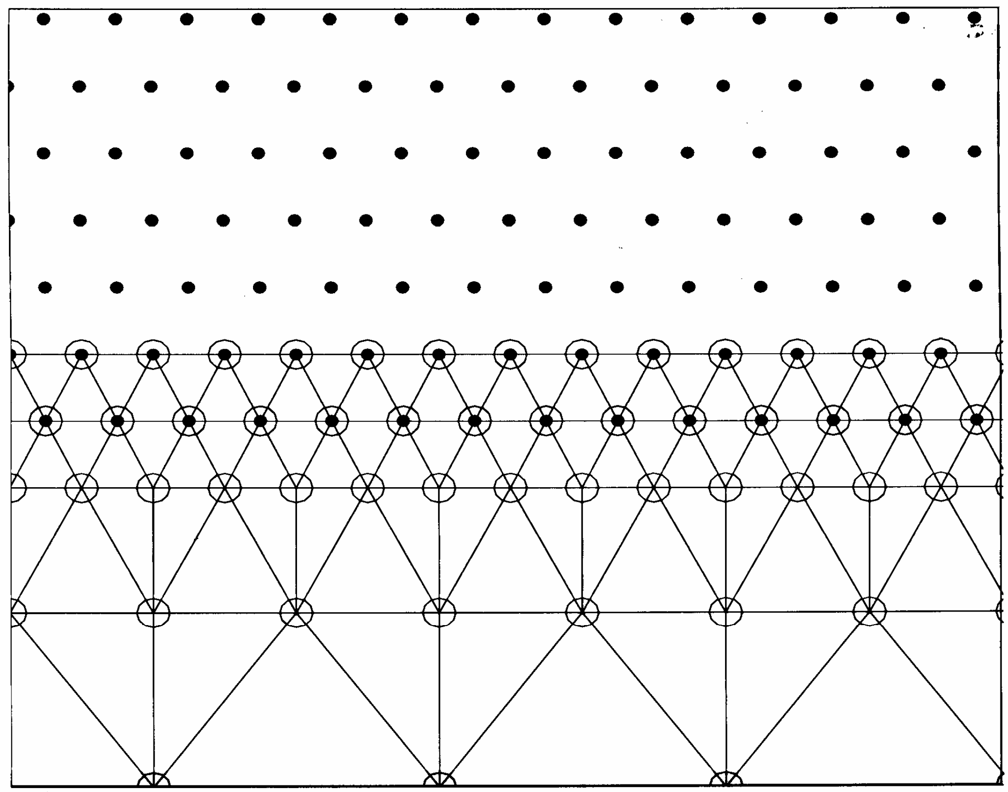


Figure by B.L. Holian and R. Ravelo, Phys. Rev. B51, 11275 (1995). Atoms are colored by velocity relative to the left-to-right local expansion velocity, which causes the crack to advance from the bottom up.

Combined MD - FEM Technique



Equations of motion:

$M_i \, d^2r_i/dt^2 = -\nabla U(r_1, r_2 \ldots . r_N)$ for MD part

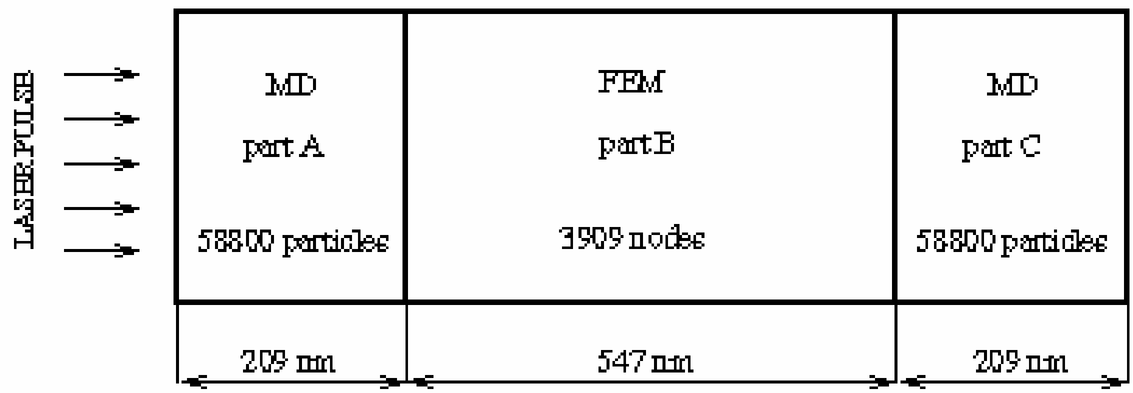
$\mathbf{[M]} \, d^2a/dt^2 = -[\mathbf{K}]\mathbf{a} + F_{ext}$ for FEM part

[**K**] and [**M**] – stiffness and mass matrices

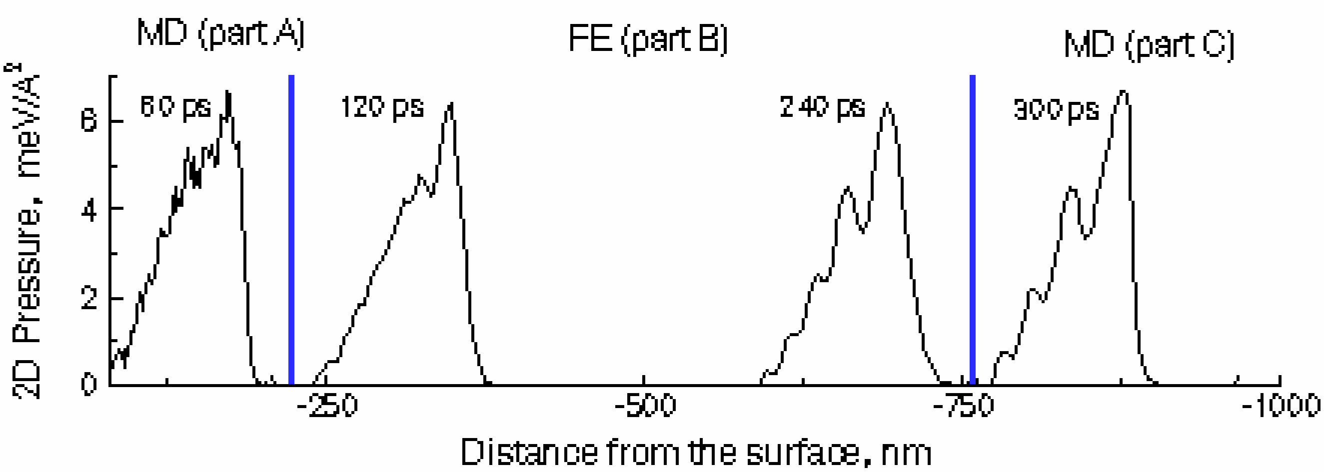
a – displacements of nodes

[**K**] is defined by the geometry of the elements and elastic moduli of material

Combined MD - FEM Technique.
Example: laser-induced pressure wave



Model system for multiscale simulation of laser ablation from μm-sized organic film



Propagation of the laser induced pressure wave from the ablation region through the successively arranged MD, FE, and another MD regions

J.A.Smirnova, L.V.Zhigilei, and B.J.Garrison, Comput. Phys. Commun., **118**, 11-16, 1999

phys. stat. sol. (b) **217**, 251 (2000)

Subject classification: 62.20.–x; 71.15.–m; S5.11; S10.1

Concurrent Coupling of Length Scales in Solid State Systems

This paper gives a good review of combined MD - FEM technique

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(Received August 10, 1999)

A strategic objective of computational materials physics is the *accurate* description of specific materials on length scales spanning the electronic to the macroscopic. We describe progress towards this goal by reviewing a seamless coupling of quantum to statistical to continuum mechanics, involving two models, implemented via parallel algorithms on supercomputers, for unifying finite elements (FE), molecular dynamics (MD) and semi-empirical tight-binding (TB). The first approach, FE/MD/TB Coupling of Length Scales (FE/MD/TB CLS), consists of a hybrid model in which simulations of the three scales are run concurrently with the minimal coupling that guarantees physical consistency. The second approach, Coarse-Grained Molecular Dynamics (CGMD), introduces an effective model, a scale-dependent generalization of finite elements which passes smoothly into molecular dynamics as the mesh is reduced to atomic spacing. These methodologies are illustrated and validated using the examples of crack propagation in silicon and the dynamics of micro-resonators. We also briefly review a number of other approaches to multiscale modeling.

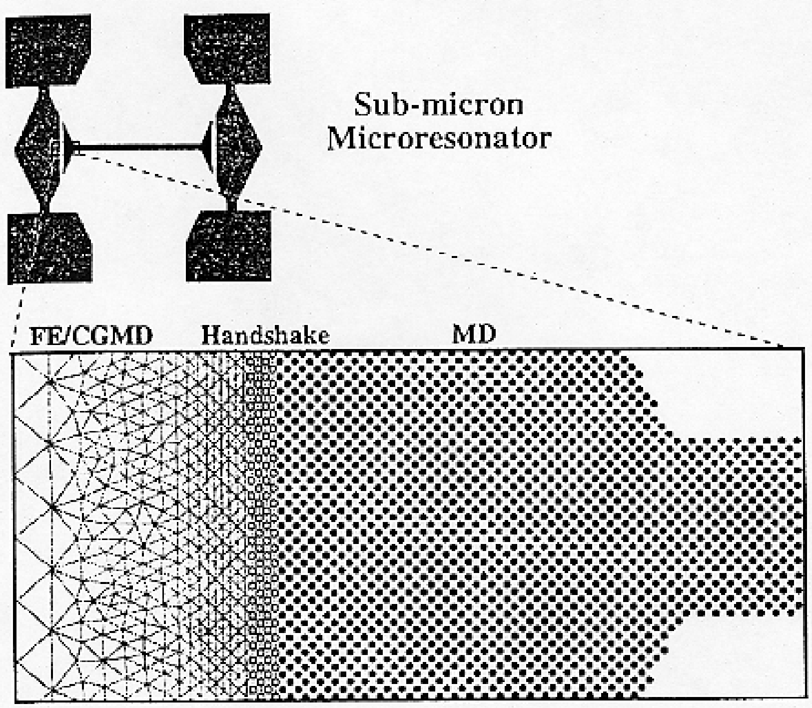
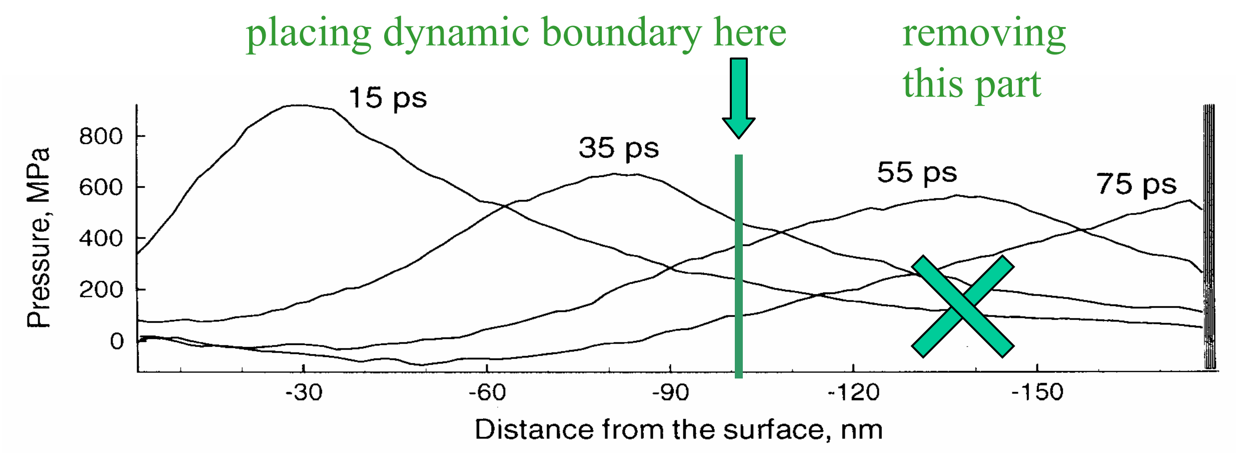


Fig. 8. Schematic diagram showing the mesh refinement used to couple length scales in the micro-resonator. An MD simulation is used in the central region of the device where the strain oscillations are the largest, while a 3D FE or CGMD simulation is used in the periphery where the strain oscillations are small. Both are run simultaneously in lock-step

Dynamic pressure-transmitting boundary condition

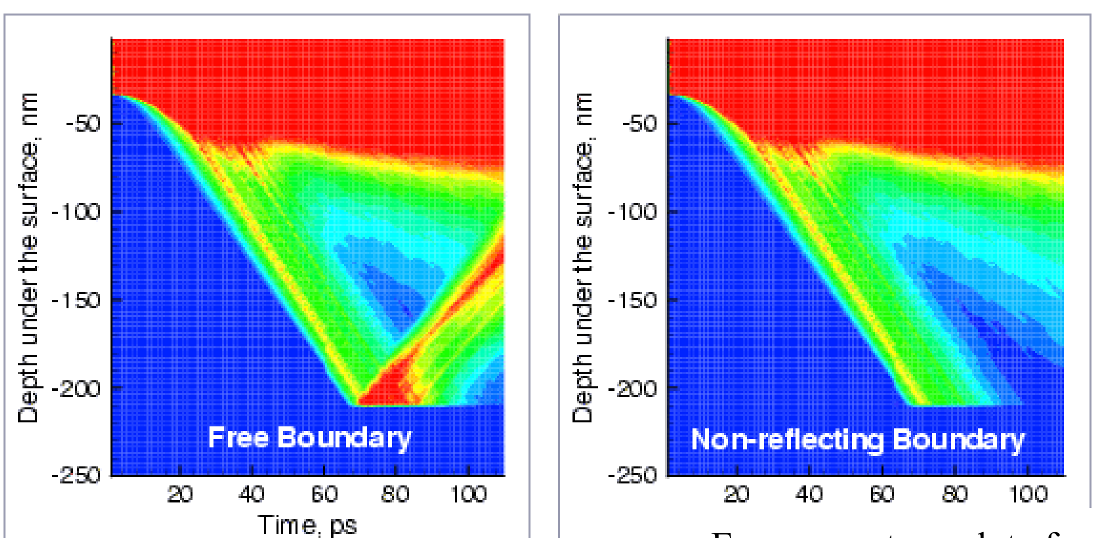
Terminating forces are applied to the particles in the boundary region to mimic the effect of the remaining material on the system of interest.

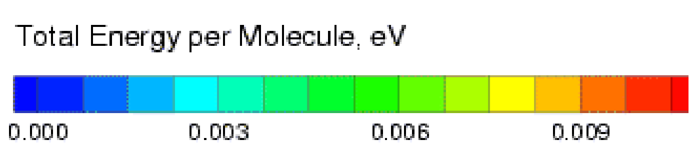


Terminating forces should account for:

- Static initial forces
- Forces due to the pressure wave propagation through the boundary region
- In the example shown above, the pressure wave results from the laser energy deposition in the surface region of the irradiated target. In this case forces due to the direct laser energy absorption in and around the boundary region during the laser pulse should be included.

Zhigilei and Garrison, Mat. Res. Soc. Symp. Proc. **538**, 491, 1999
Schäfer, Urbassek, Zhigilei, Garrison, Comp. Mater. Sci. **24**, 421, 2002

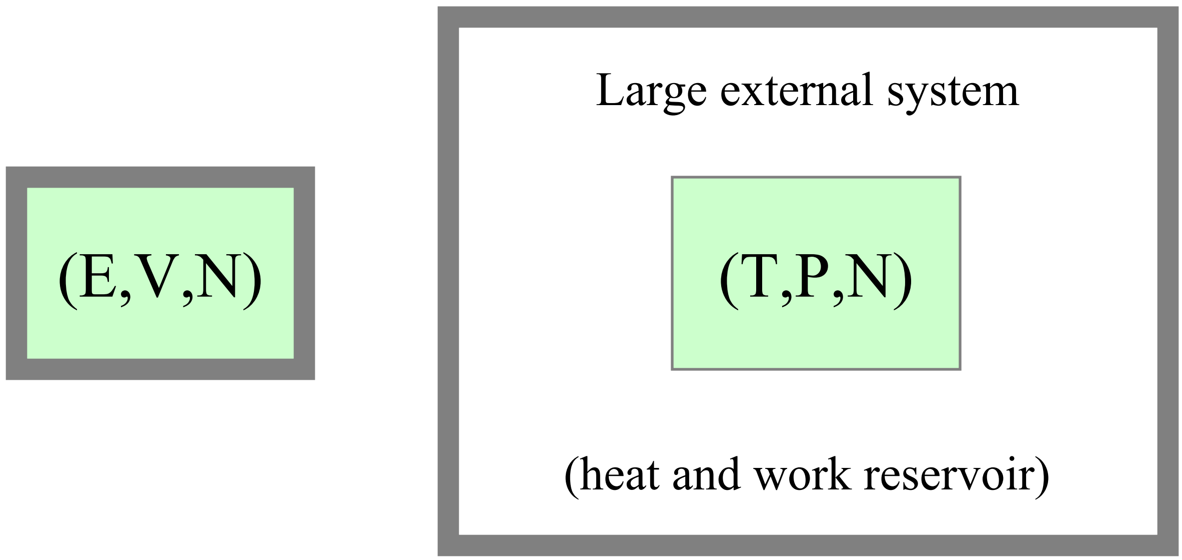




Energy contour plots for free & non-reflecting boundary conditions applied at the bottom of the computational cell. Energy is deposited to a surface region by a short laser pulse.

The extended system method: **See handouts on constant P and T methods**

The total energy of the system is allowed to fluctuate due to the exchange of work or/and heat between the MD simulation cell and an extended system.



Constant P:

The idea of the extended system method was first proposed by Andersen [J. Chem. Phys. **72**, 2384 (1980)] for constant pressure simulations. The method provides the exchange of work between the computational cell and an external system.

Constant T:

The extended system method for constant temperature simulation is originally proposed by Nosé [J. Chem. Phys. **81**, 511 (1984)] and reformulated by Hoover [Phys. Rev. A **31**, 1695 (1985)]. The total energy of the computational cell is allowed to fluctuate due to the thermal contact with a heat bath.