Condensed Matter Physics

Molecular dynamics I.

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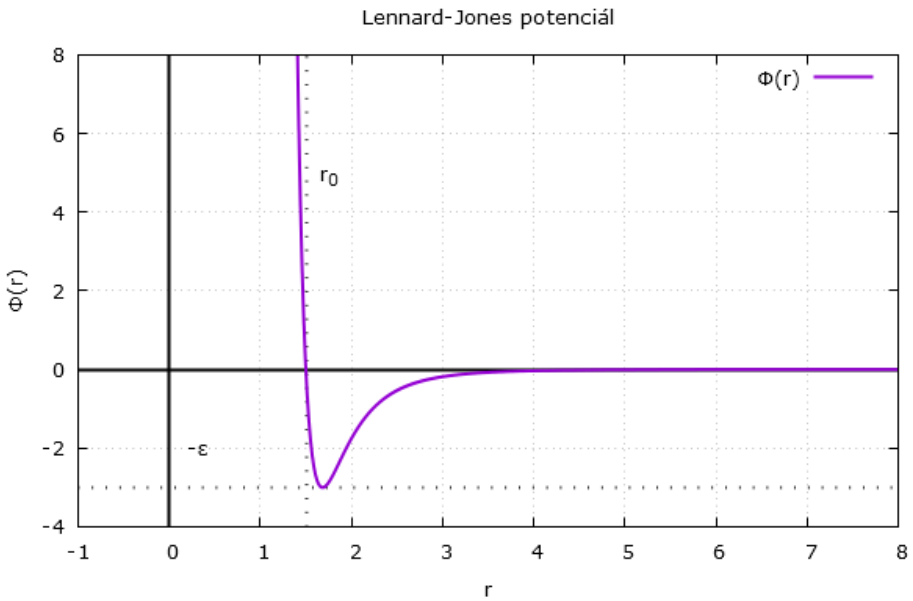
Empirical potentials

Pair energy

$$E_p = \sum_{i<j} \phi\left(\vec{r}_i - \vec{r}_j\right) \qquad \phi(r, A, B, \ldots)$$



Lennard-Jones potential with $r_0 = 1.5$ and $\varepsilon = 3$.

$$\phi(r) = 4\varepsilon\left(-\frac{r_0^6}{r^6} + \frac{r_0^{12}}{r^{12}}\right) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

Empirical potentials

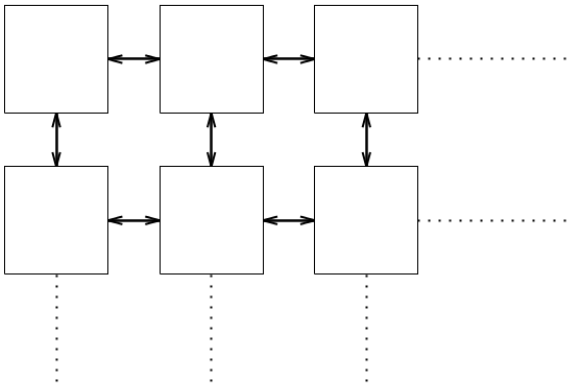
Forces (central force field)

$$\vec{F}_{ij} = \frac{\mathrm{d}\phi(r_{ij})}{\mathrm{d}r} \frac{\vec{r}_i - \vec{r}_j}{r_{ij}}$$

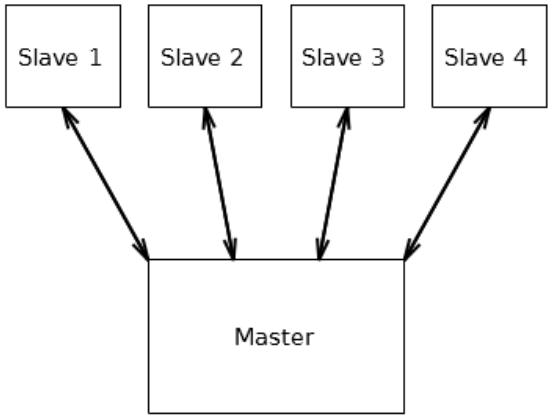
Equation of motions

$$\ddot{\vec{r}}_i = \frac{1}{m_i} \sum_{i \neq j}^{N} \vec{F}_{ij}$$

Numerical solution on parallel computers
Array processors



Master Slave



A master-slave code

Master

- Slave Boot
- Send(X)
- Receive-force
- Sum-force
- Update X

Slave

- Receive X
- Forcecalc
- Send-force

Cluster rotation

angular momentum

$$\vec{L} = \sum_{i=1}^{N} m_i \left(\vec{r}_i \times \vec{v}_i\right)$$

angular speed

$$\vec{L} = \hat{I}\vec{\omega}$$

moment of inertia

$$\hat{I} = \sum_{i=1}^{N} m_i \begin{pmatrix} y_i^2 + z_i^2 & -x_i y_i & -x_i z_i \\ -x_i y_i & y_i^2 + z_i^2 & -y_i z_i \\ -x_i z_i & -y_i z_i & x_i^2 + y_i^2 \end{pmatrix}$$

from these

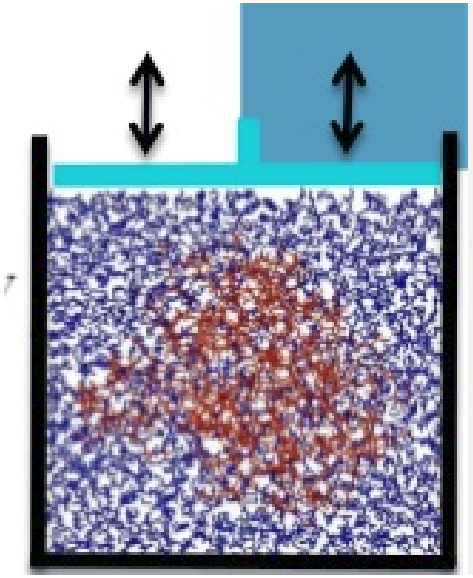
$$\vec{\omega} = \hat{I}^{-1}\vec{L}$$

the velocities are corrected with a rigid body rotation

$$\vec{v}_i' = \underline{v}_i - \left(\vec{\omega} \times \vec{r}_i\right)$$

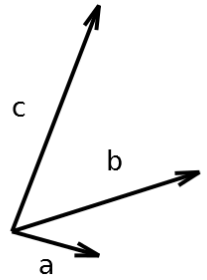
External constrains, pressure

One can add an “external” piston



Nosé Hoover barostat

Periodic boundary condition



$$\hat{h} = \begin{pmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{pmatrix}$$

The volume of the parallelepiped

$$\Omega = \det \hat{h}$$

Let us introduce relative coordinates s_i

$$\vec{r}_i = \hat{h}\vec{s}_i$$

the scalar product is

$$(\vec{r}_i, \vec{r}_j) = (\hat{h}\vec{s}_i, \hat{h}\vec{s}_i) = (\vec{s}_i, \hat{h}^* \hat{h}\vec{s}_i) = (\vec{s}_i, \hat{G}\vec{s}_i)$$

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The Lagrangian of the system

$$L = T - U$$

where T is the kinetic energy and U is the potential energy.

$$L_0 = \frac{1}{2}\sum_i m_i \dot{\vec{s}}_i \hat{G} \dot{\vec{s}}_i - \sum_{i<j} \phi\left(\hat{h}(\vec{s}_i - \vec{s}_j)\right) - p_{\text{ext}}\Omega$$

Some thermodynamics

$$U(S,V) \to H(S,p) = U + pV$$

New Lagrangian with general coordinate $\hat{h}$

$$L_1 = \frac{1}{2}\sum_i m_i \dot{\vec{s}}_i \hat{G} \dot{\vec{s}}_i - \sum_{i<j} \phi\left(\hat{h}(\vec{s}_i - \vec{s}_j)\right) - p_{\text{ext}}\Omega + \frac{1}{2} W \mathrm{Tr}\left(\dot{h}^* \dot{h}\right)$$

where W is a mass.
Euler-Lagrange equations

$$\frac{d}{dt}\frac{dL}{d\dot{q}_i} - \frac{dL}{dq_i} = 0$$

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Equation of motions

$$m\frac{d}{dt}(\hat{G}\dot{\vec{s}}_i) - \hat{h}\left(\sum_{j\neq i}\vec{F}_{ij}\right) = 0$$

that is

$$m(\hat{G}\ddot{\vec{s}}_i) + m\dot{\hat{G}}\dot{\vec{s}}_i - \hat{h}\left(\sum_{j\neq i}\vec{F}_{ij}\right) = 0$$

Let us consider for $\hat{h}$

$$\frac{d}{dh_{lm}}(h_{ij}\dot{s}_j h_{ik}\dot{s}_k) = \delta_{li}\delta_{mj}\dot{s}_j h_{ik}\dot{s}_k + h_{ij}\dot{s}_j\delta_{li}\delta_{mk}\dot{s}_k = h_{lk}(\dot{\vec{s}}\circ\dot{\vec{s}})_{km} = \frac{1}{\Omega}[(\vec{v}\circ\vec{v})\sigma]_{lm}$$

with

$$\hat{\sigma} = \begin{pmatrix} \vec{b}\times\vec{c} \\ \vec{c}\times\vec{a} \\ \vec{a}\times\vec{b} \end{pmatrix}$$

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Equation of motion for $\hat{h}$

$$\ddot{\hat{h}} = \frac{1}{W}\left(\hat{\pi} - p_{\text{ext}}\right)\hat{\sigma}$$

with

$$\hat{\pi} = \frac{1}{\Omega}\left(\sum_{i=1}^{N} m_i \dot{\vec{r}}_i \circ \dot{\vec{r}}_i - \sum_{i<j}^{N} \vec{F}_{ij} \circ \left(\vec{r}_i - \vec{r}_j\right)\right)$$

Stationer state if

$$\hat{\pi} - p_{\text{ext}} = 0$$

Clausius virial theorem

$$\left\langle \frac{df}{dt} \right\rangle = \frac{f(t_2) - f(t_1)}{t_2 - t_1} \to 0$$

Let us consider

$$m\left\langle \frac{d\dot{\vec{r}}\vec{r}}{dt} \right\rangle = m\left\langle \dot{\vec{r}}\dot{\vec{r}} \right\rangle + m\left\langle \ddot{\vec{r}}\vec{r} \right\rangle = 2\left\langle E_{kin} \right\rangle + \left\langle \vec{r}\vec{F} \right\rangle = 0$$

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Pressure

$$-p\int_{\partial\Omega}\vec{r}d\vec{A} = -p\int div(\vec{r})d\Omega = -3p\Omega$$

How to select W

$$W = ? \qquad \frac{M}{10}$$

Oscillation: relaxation time

$$\tau = 2\pi\sqrt{\frac{W}{3LK}} \qquad \text{Nose, Klein}$$

Damping

$$\dot{\vec{\hat{h}}}' = \dot{\vec{\hat{h}}}(1-\beta) \qquad 0 \leq \beta \leq 1$$

Temperature control

I. velocity re-scaling

$$\frac{3}{2}k_B T = \frac{m}{2}\left\langle v^2 \right\rangle$$

II. Langevin thermostat

Equation of motions

$$m\ddot{\vec{r}}_i = \vec{F}_i - \gamma\dot{\vec{r}}_i + \delta\vec{W}_i(t)$$

where $\delta\vec{W}_i$ is a random force with

$$\frac{1}{3}\left\langle \delta\vec{W}_i(t)\delta\vec{W}_j(t') \right\rangle = \delta_{ij}\delta(t-t')2mk_b T\gamma$$

Let us consider the simple Langevin equation

$$\dot{v} = -\gamma v + \sigma\delta W(t) \;\text{ with }\; \langle \delta W(t) W(t') \rangle = \delta(t-t')$$

The corresponding Fokker Planck equation for $P(v,t)$

$$\frac{\partial P}{\partial t} = \gamma'\partial_v(vP) + \frac{\sigma^2}{2}\partial_v\partial_v P$$

Temperature control

Stationer solution

$$\gamma' P_\infty(v) v = -\frac{\sigma^2}{2} \partial_v P_\infty(v)$$

Leading to

$$P_\infty(v) = p_0 e^{-\frac{\gamma' v^2}{\sigma^2}}$$

It should be the Boltzmann distribution

$$P_\infty(v) = p_0 e^{-\frac{mv^2}{2k_b T}}$$

leading to the fluctuation dissipation theorem

$$\sigma = \sqrt{2\gamma' k_B T / m}$$

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scaling of time

$$t' = st$$

where s is a scale factor.
The original Lagrangian

$$L = \sum_i^N \frac{1}{2} m_i v_i^2 - V(\vec{r}_1, \dots \vec{r}_N)$$

with s depending on t'

$$L' = s^2 \sum_i^N \frac{1}{2} m_i v_i'^2 - V(r_1, \dots r_N) + \frac{1}{2} A \dot{s}^2 - N f k_B T \ln(s)$$

Equation of motion

$$s^2 m_i a_i' = -\frac{\partial V}{\partial r_i} - 2\dot{s} s m_i v_i'$$

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$$A\ddot{s} = -2s\sum_i \frac{1}{2}m_i v_i'^2 + Nfk_b T\frac{1}{s}$$

$$As\ddot{s} = Nfk_B T - \sum_i \frac{1}{2}m_i v_i^2$$

We also have a friction like term

$$m_i a_i = -\frac{\partial V}{\partial r_i} - 2\dot{s}m_i v_i$$

Equipartition theorem

$$A\ddot{s} = \frac{1}{2s}\left\{Nf\frac{k_B T}{2} - \frac{1}{2}m_i v_i^2\right\}$$

Examples

Diffusion

$$D = \lim_{t\to\infty} \frac{\langle R^2(t)\rangle}{2\mathrm{d}t}$$

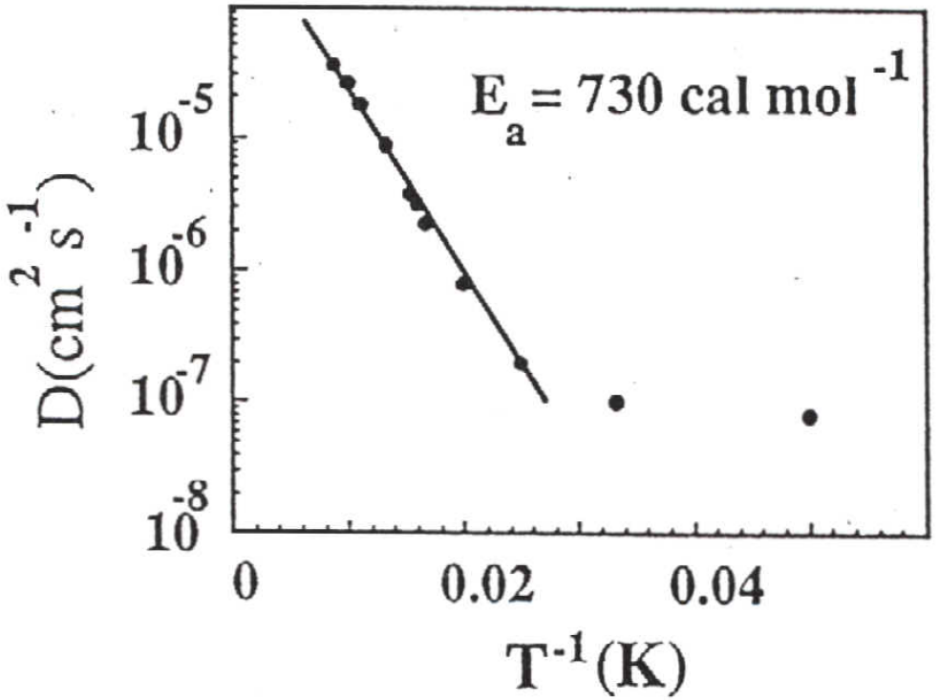

Figure: Arrhenius plot of self-diffusion coefficient for the Lennard-Jones model

Examples

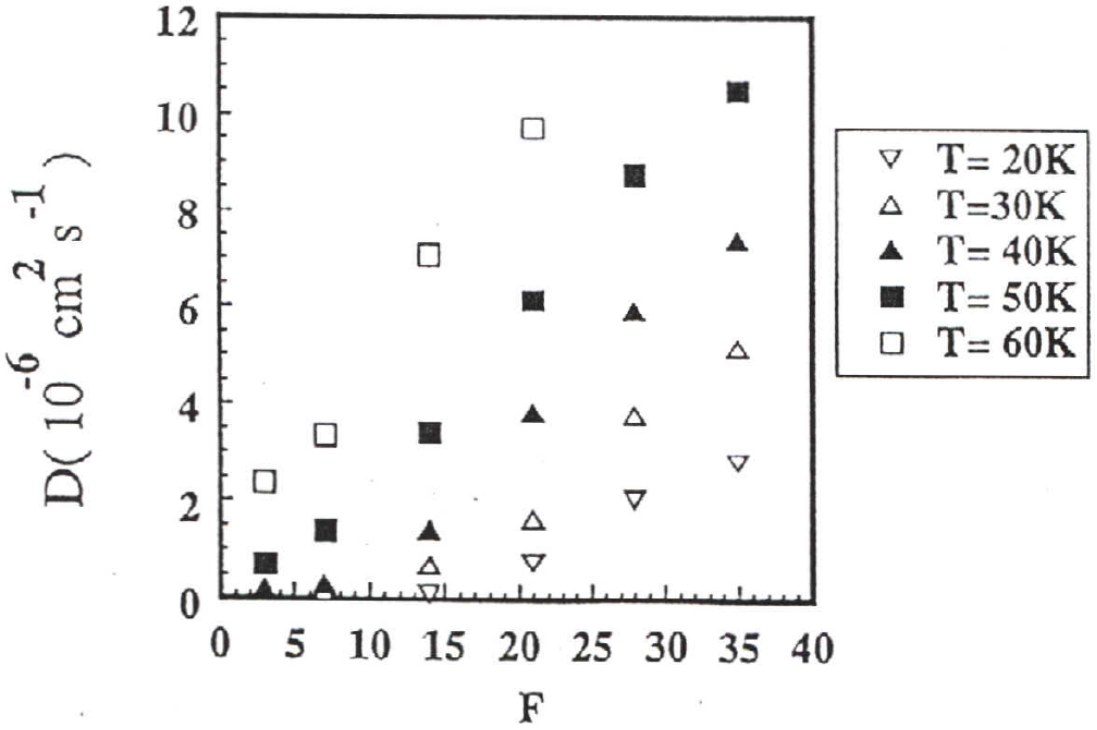

Figure: Diffusion D vs. external force in the LJ model. For the definition of F see text.

Examples

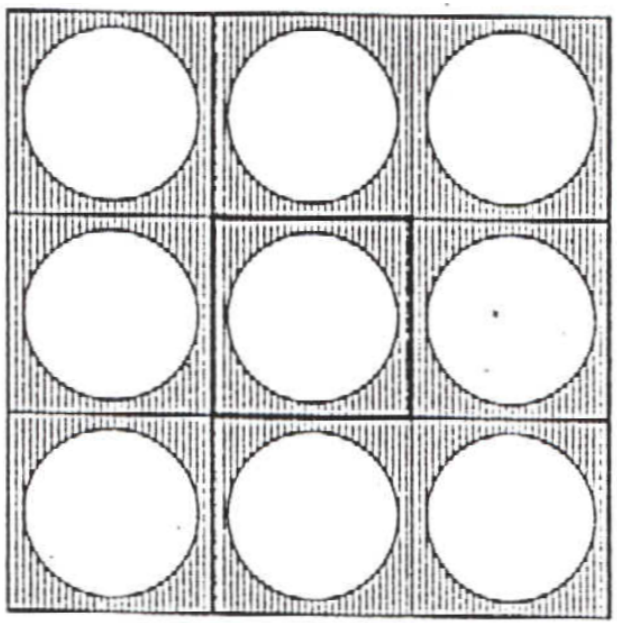

Figure: To illustrate the geometry of the simulaton of grain boundary motion. Born-von Karman periodic border conditions are applied in all 3 directions to a rectangular cell containing a cylinder of misoriented material.

Examples

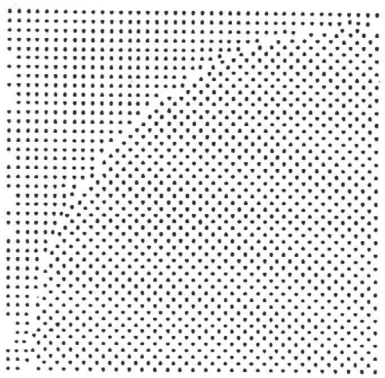

Figure: The top left quadrant of the cell showing the relaxed atomic structure at $T = 0\ K$

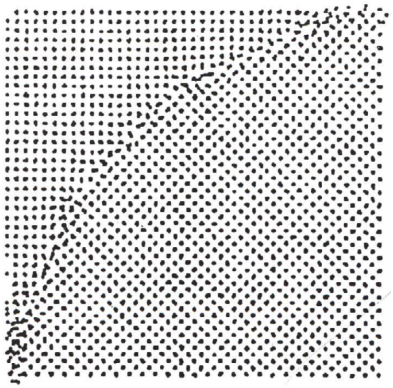

Figure: The top left quadrant of the cell showing a snap shot of the atomic structure at $T = 600\ K$

Examples

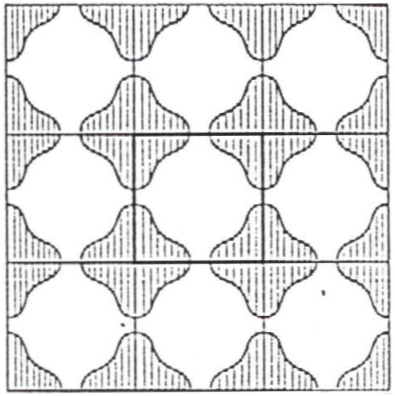

Figure: Schematic illustration of the unexpected motion of the boundaries defining the cylinders shown in fig. 3

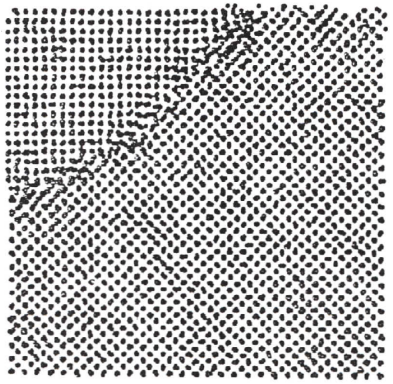

Figure: A snap shot of the cell at $T = 1200\ K$. The boundary is migrating to the top left corner of the cell quadrant

Examples

Crack propagation

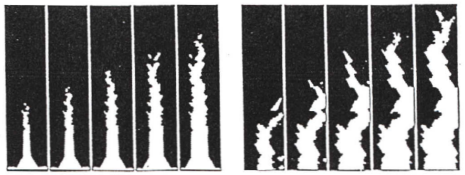

Figure: a) The onset of crack instability, in reduced time intervals of 7 and beginning at reduced time 85. b) Last zigzag propagation, in reduced time intervals of 7 and beginning at reduced time 220.

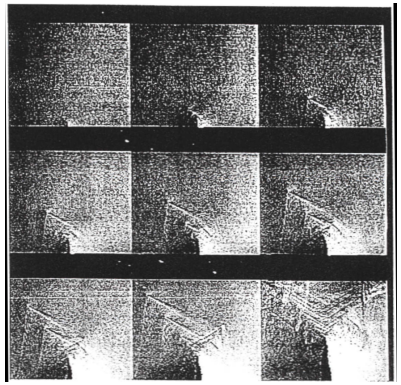

Figure: The time evolution of the propagating embedded-atom crack using a grey-scale rendering of the instantaneout l

Examples

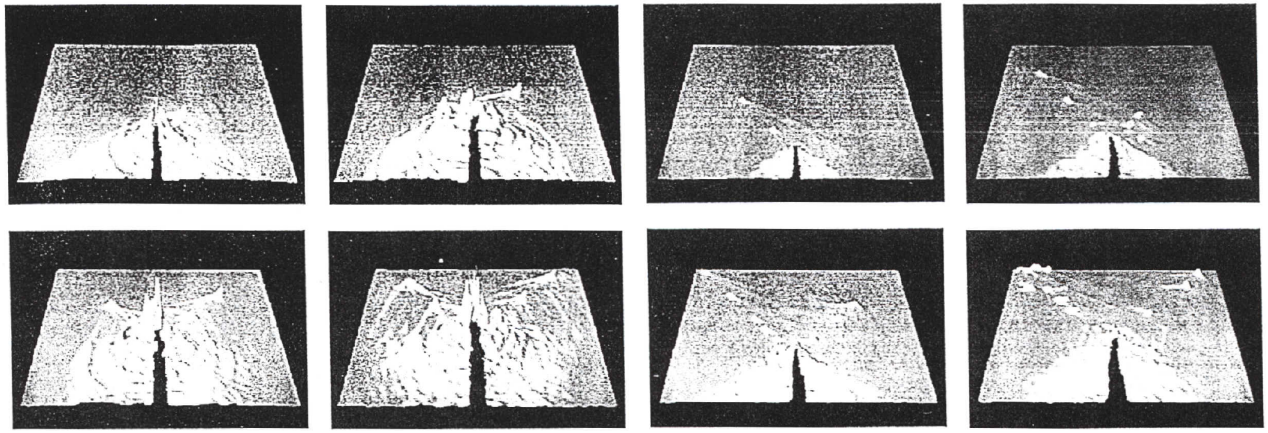

Figure: The temperature evolution of the propagating crack using grey scale rendering of the instantenous local kinetic energy of the atoms which goes from dark grey (colt) to white (hot), where the hottest temperature $\frac{k_B T}{c}$ is less than 0.1. The time sequence goes from left to right and top to bottom. The top four frames describe the Lennard-Jones solid, and the frames are for reduced times 200, 225, 250 and 275. the bottom four frames describe the embedded-atom solid, and the frames are for reduced times 250, 300, 325 and 350.

Examples

MD simulation with 10^9 atoms!