Ab initio methods in solid state physics
XII. Molecular Dynamics

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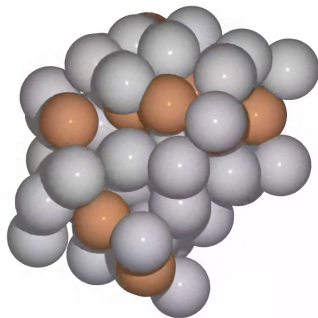
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May 16, 2023

Molecular dynamics

- Why?
- Basic idea
- The devil in the details
- Approximations
- NVE, NVT, NPT, ...
- Goals

First attempts

Phase Transition for a Hard Sphere System

B. J. ALDER AND T. E. WAINWRIGHT

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(Received August 12, 1957)

A CALCULATION of molecular dynamic motion has been designed principally to study the relaxations accompanying various nonequilibrium phenomena. The method consists of solving exactly (to the number of significant figures carried) the simultaneous classical equations of motion of several hundred particles by means of fast electronic computors. Some of the details as they relate to hard spheres and to particles having square well potentials of attraction have been described.[1,2] The method has been used also to calculate equilibrium properties, particularly the equation of state of hard spheres where differences with previous Monte Carlo[3] results appeared.

Dynamics of Radiation Damage*

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(Received July 14, 1960)

Radiation damage events at low and moderate energies (up to 400 ev) are studied by machine calculations in a model representing copper. Orbits of knock-on atoms are found and the resulting damaged configurations are observed to consist of interstitials and vacancies. Thresholds for producing permanently displaced atoms (i.e., interstitials) are about 25 ev in the $\langle 100 \rangle$ direction, 25 to 30 ev in the $\langle 110 \rangle$ direction, and around 85 ev in the $\langle 111 \rangle$ direction. Collision chains in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions are prominent; at low energies the chains focus, at higher energies they defocus. Above threshold, the chains transport matter, as well as energy, and produce an interstitial at a distance. The range of $\langle 110 \rangle$ chains has been studied in detail. Localized vibrational modes associated with interstitials, agitations qualitatively like thermal spikes, ring annealing processes, and a higher energy process somewhat like a displacement spike have been observed. Replacements have been found to be very numerous.

The configurations of various static defects have also been studied in this model. The interstitial is found to reside in a "split" configuration, sharing a lattice site with another atom. The crowdion is found not to be stable, and Frenkel pairs are stable only beyond minimum separations, which are found to be very much dependent on orientation.

Why?

- MC is faster
- MC needs $p(x)$
- Temperature?
- MD has $T = \langle E_k \rangle$
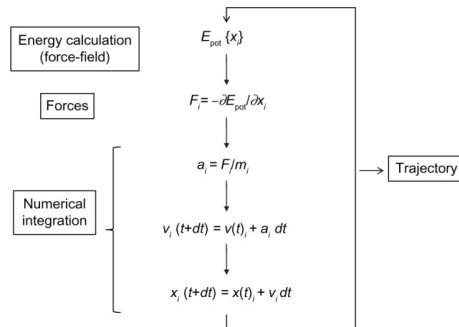- No need for $p(x)$
- Dynamical effects
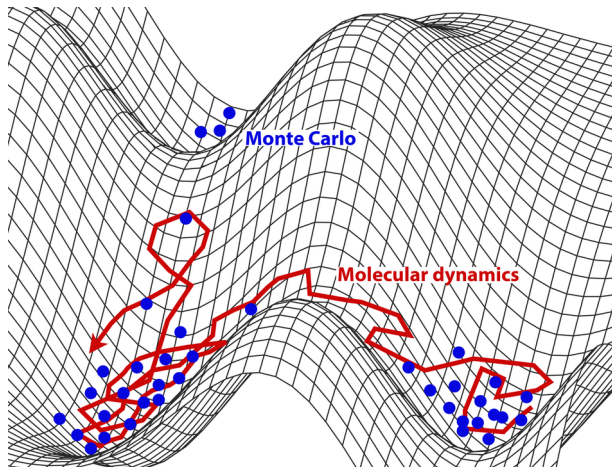
Basic idea

The basic idea behind molecular dynamics is simple: solve the numerically solve equation of motion (EOM) for the system and derive its properties from analysis of the calculated trajectory.
The equation of motion for the i-th atom reads:

$$\frac{d^2\mathbf{x}_i}{dt^2} = \frac{\mathbf{F}_i}{m_i}$$

Velocity Verlet I

Calculate positions to higer order and velocities at half step.

$$\vec{x}(t + \Delta t) = \vec{x}(t) + \vec{v}(t)\,\Delta t + \frac{1}{2}\,\vec{a}(t)\Delta t^2,$$

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{\vec{a}(t) + \vec{a}(t + \Delta t)}{2}\Delta t$$

This algorithm assumes that acceleration $\vec{a}(t + \Delta t)$ only depends on position $\vec{x}(t + \Delta t)$ and does not depend on velocity $\vec{v}(t + \Delta t)$.

Velocity Verlet II

1. $\vec{v}\left(t + \frac{1}{2}\,\Delta t\right) = \vec{v}(t) + \frac{1}{2}\,\vec{a}(t)\,\Delta t.$

2. $\vec{x}(t + \Delta t) = \vec{x}(t) + \vec{v}\left(t + \frac{1}{2}\,\Delta t\right)\,\Delta t.$

3. $\vec{a}(t + \Delta t)$ at $\vec{x}(t + \Delta t).$

4. $\vec{v}(t + \Delta t) = \vec{v}\left(t + \frac{1}{2}\,\Delta t\right) + \frac{1}{2}\,\vec{a}(t + \Delta t)\Delta t.$

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Shortened by eliminating the half-step velocity:

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2. $\vec{a}(t + \Delta t)$ at $\vec{x}(t + \Delta t)$.

3. $\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{1}{2}\left(\vec{a}(t) + \vec{a}(t + \Delta t)\right)\Delta t.$

The devil in the details

- What about electrons?
- Time step selection.
- PBC/box/vacuum.
- $N(N-1)/2$ scaling.
- Error propagation and growth.
- Pressure, Temperature, Energy.
- Time scale, thermalisation.

Approximations

1. Born-Oppenheimer approximation
   - electrons are light,
   - nuclei are classical
2. Timestep
   - $\approx 1/40$ of periods
   - $\Delta x < 1/20(x_i - x_j)$
3. Scaling
   - No penalty in DFT
   - Interaction range limit

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1. Born-Oppenheimer approximation
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   - $\approx 1/40$ of periods
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3. Scaling
   - No penalty in DFT
   - Interaction range limit
4. Error propagation
   - small Δt
   - Thermal bath
5. N, V, P, T, E
   - Energy rescaling
   - Nosé–Hoover thermostat
   - Parrinello-Rahman barostat
   - Langevin dynamics
6. Thermalisation
   - Relaxation time, energy distribution

Goals

- Dynamical processes
- Phase transitions
- Vibrational spectra
- Phase space sampling
- Reaction kinetics
- Parameter extraction
- Model validation