MOLECULAR DYNAMICS: PAIR DISTRIBUTION FUNCTION

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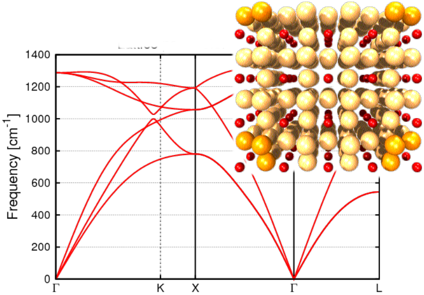
Why use Molecular Dynamics simulations?

- Simulate thermodynamic processes with large particle numbers
- Calculate vibrational/Phonon spectra



[1]https://patrickmiguelbishop.files.wordpress.com/2011/06/melt1.jpg
[2]http://departments.kings.edu/chemlab/animation/reoxnew.gif
[3]http://exciting.wdfiles.com/local--files/lithium-phonon-and-thermal-properties-diamond/c-phonon-dispersion-conv.png

Contents

Velocity-Verlet Method

describe motion of particles via their coordinates and velocities:

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 \tag{1}$$

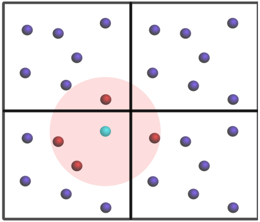
$$v(t+\Delta t) = v(t) + \frac{\Delta t}{m}\left(\frac{f_i(t) + f_i(t+\Delta t)}{2}\right) \tag{2}$$

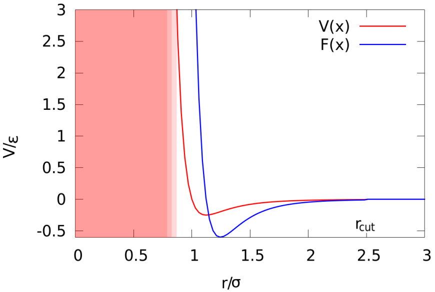
Advantages:

- error $\mathcal{O}(\Delta t^3)$ for both quantities
- time-reversible

Minimum Image Convention

- Periodic Boundaries: reduce nr. of particles but infinite nr. of interaction partners
- Minimum image: Reducing amount of calculations to $\mathcal{O}(N^2)$
- Is valid, if the box is larger than twice the length of potential

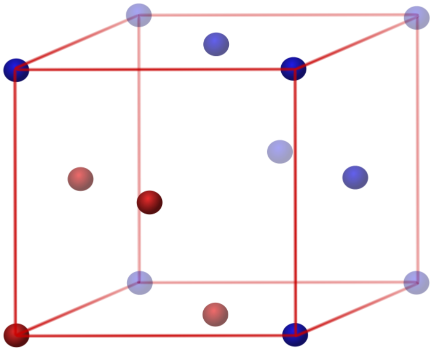




The system of interest

Argon-crystal (fcc-lattice)

- density: $\rho = 1.8 \frac{g}{cm^3}$
  $\rho = 0.6 \frac{g}{cm^3}$
- $T \in [20; 520]$ K



Thermostate

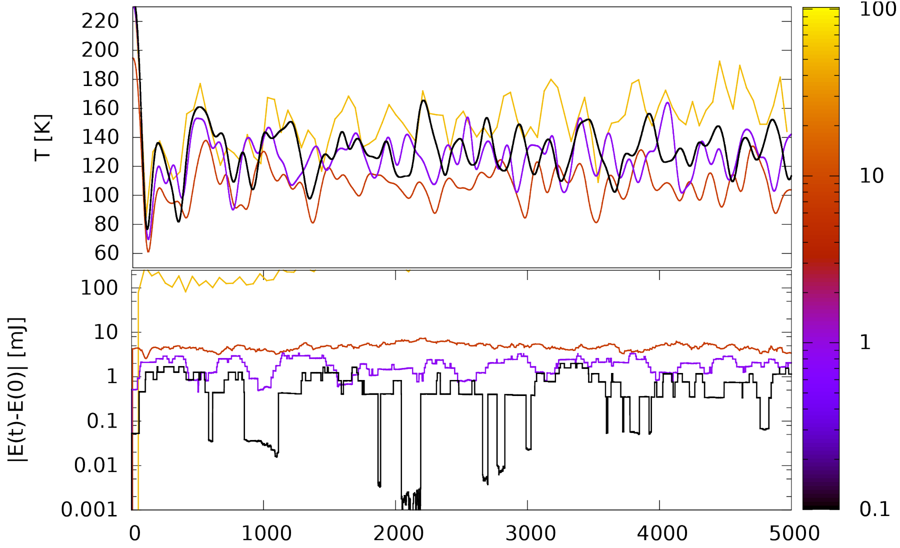
Starting conditions

1. $r_{\mathrm{i}}(0) = r_{\mathrm{i,eq}}$
2. $v_{\mathrm{i}}(0) = rand(-1;1) \cdot \sqrt{k_B T}$

To keep control over temperature: introduce thermostate (weak velocity rescaling)

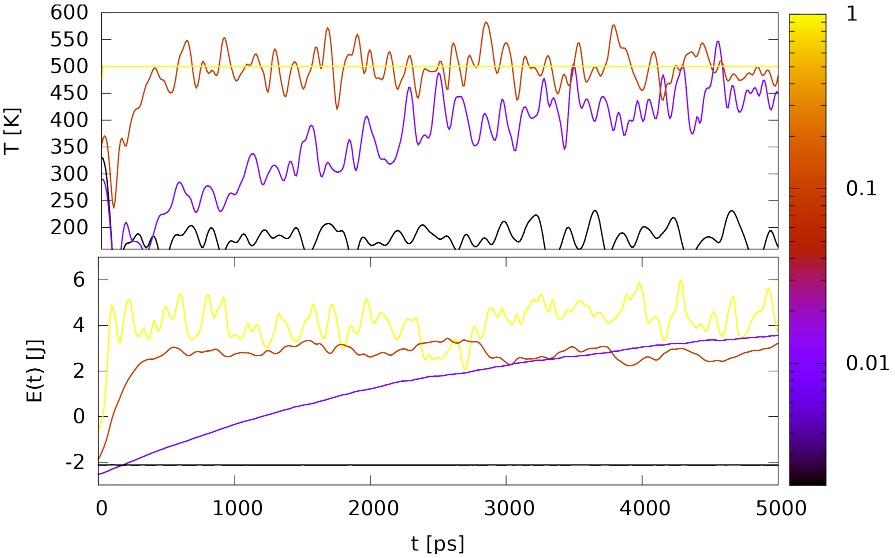
$$v(t) = v(t)\sqrt{\frac{T_{\mathrm{req}}}{T_{\mathrm{sys}}}\alpha + (1-\alpha)v(t)}$$

Reliability of the code I



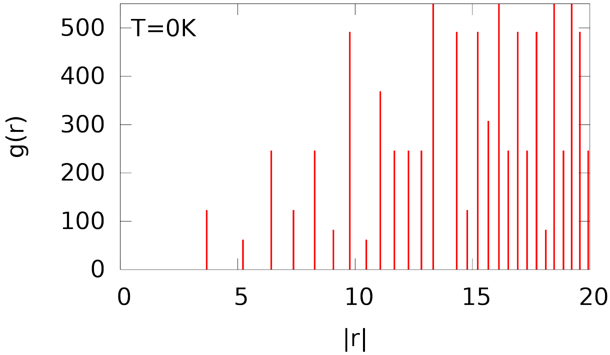
colour bar: time step [ps]

Reliability of the code II



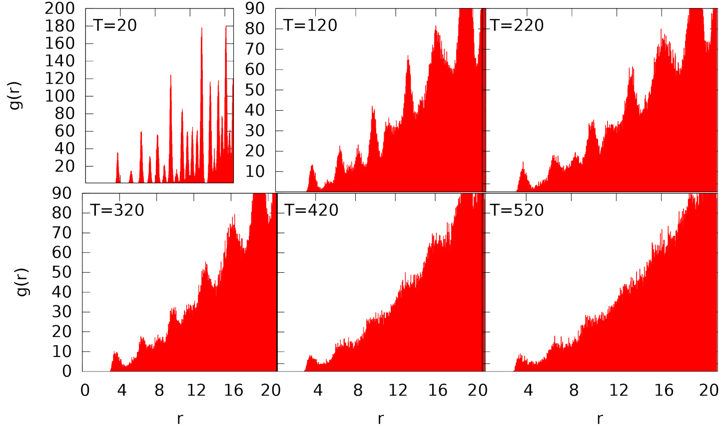
Thermodynamics I: melting

consider the dense system: $\rho = 1.8\,\frac{g}{cm^3}$
pair distribution function: $g(r) = \rho(r)/\rho_0$
for fcc-lattice (0 K):

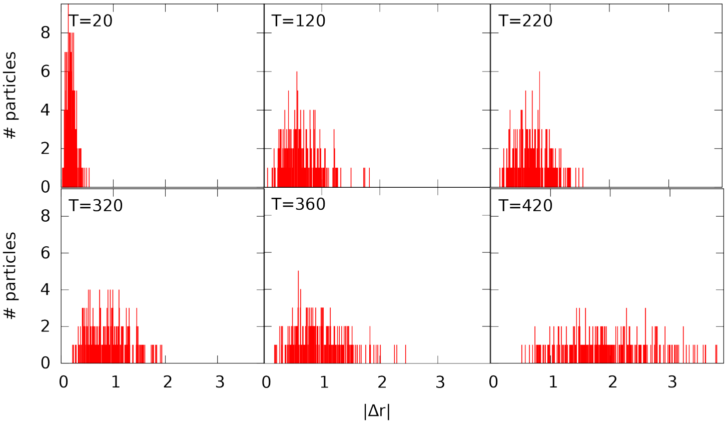


melting: visible as loosing structure in $g(r)$

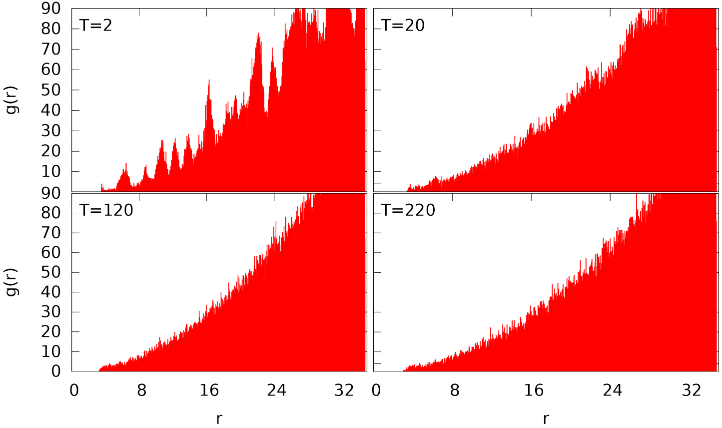
Thermodynamics II



Thermodynamics III



Thermodynamics IV: low density



Discussion and Outlook

- velocity-Verlet is capable and efficient for describing large systems
- velocity-rescaling gives easy but reliable thermostate

- The melting point was not found properly
  - Use density in between
  - Use other potential (Morse)
  - Find further quantities to specify melting point

Thank you for your attention

Order of velocity-Verlet

$$r_i(t+\Delta t) = r_i(t) + v_i(t)\Delta t + a_i(t)\frac{\Delta t^2}{2} + \mathcal{O}(\Delta t^3)$$

$$v_i(t+\Delta_t) = v_i(t) + \dot{v}_i(t)\Delta t + \ddot{v}_i(t)\frac{\Delta t^2}{2} + \mathcal{O}(\Delta t^3)$$

$$\dot{v}_i(t) = \frac{1}{m} f_i(t) \qquad \ddot{v}_i(t) = \frac{1}{m}\dot{f}_i(t) = \frac{1}{m}\frac{-f_i(t) + f_i(t+\Delta t)}{\Delta t} + \mathcal{O}(\Delta t)$$

$$\begin{aligned} v_i(t+\Delta_t) &= v_i(t) + \frac{1}{m}\left(f_i(t)\Delta t + \frac{-f_i(t) + f_i(t+\Delta t)}{\Delta t}\frac{\Delta t^2}{2}\right) + \mathcal{O}(\Delta t^3) \\ &= v_i(t) + \frac{\Delta t}{m}\left(\frac{f_i(t) + f_i(t+\Delta t)}{2}\right) + \mathcal{O}(\Delta t^3) \end{aligned}$$

Time-reversibility

to be shown: $r_i(t + \frac{\Delta t}{2}) = r_i\left((t + \Delta t) - \frac{\Delta t}{2}\right)$:

$$r(t + \frac{\Delta t}{2}) = r(t) + v(t)\frac{\Delta t}{2} + \frac{f(t)}{2m}\frac{\Delta t^2}{4}$$

$$r((t + \Delta t) - \frac{\Delta t}{2}) = r(t + \Delta t) - v(t + \Delta t)\frac{\Delta t}{2} + \frac{f(t + \Delta t)}{2m}\frac{\Delta t^2}{4}$$

use:

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2$$

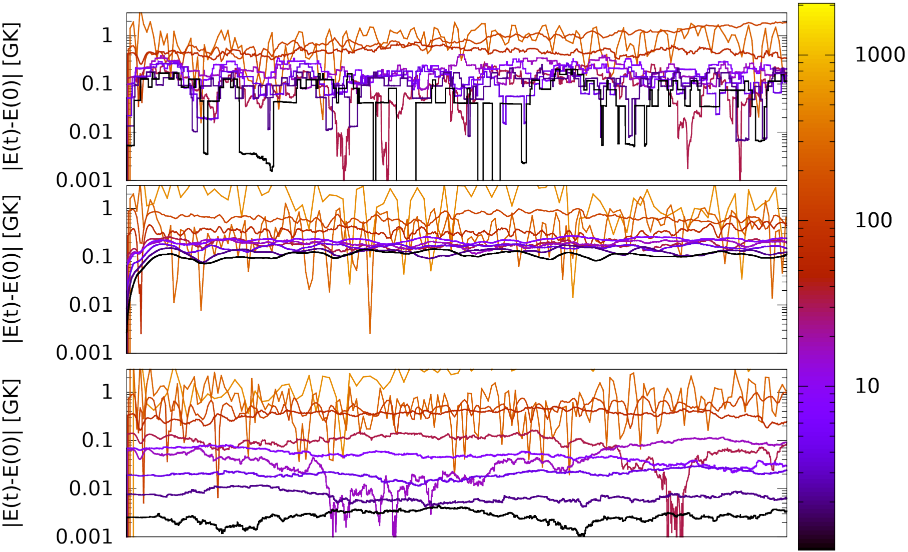
$$v(t + \Delta t) = v(t) + \frac{\Delta t}{2}\left(\frac{f_i(t) + f_i(t + \Delta t)}{2}\right)$$

Time-reversibility

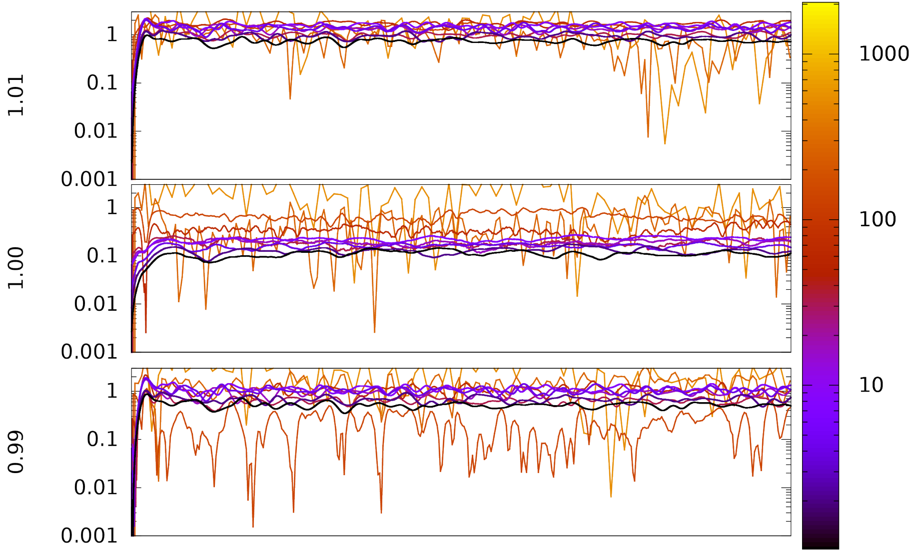
inserting yields

$$
\begin{aligned}
r((t+\Delta t)-\frac{\Delta t}{2}) &= r(t)+v(t)\Delta t+\frac{f(t)}{2m}\Delta t^2 - \\
&\left(v(t)+\frac{\Delta t}{2}\left(\frac{f_i(t)+f_i(t+\Delta t)}{2}\right)\right)+\frac{f(t+\Delta t)}{2m}\frac{\Delta t^2}{4} \\
&= r(t)+v(t)\frac{\Delta t}{2}+\frac{f(t)}{2m}\frac{\Delta t^2}{2}-\frac{f(t+\Delta t)}{2m}\frac{\Delta t^2}{4} \\
&= r(t)+v(t)\frac{\Delta t}{2}+\frac{f(t)}{2m}\frac{\Delta t^2}{4}
\end{aligned}
$$

Energy conservation: Cutoff



Energy conservation: Source of Fluctuation



error in energy is numerical; not due to overpronounciation of one of its parts