8. Basics of QMD simulations

- combination of DFT and MD is possible in Born-Oppenheimer approximation:
  - Electrons are treated quantum mechanically on the level of the Schrödinger equation (KS equations):
    \[
    \left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{KS}(\vec{r}) \right] \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})
    \]
  - Ions are treated classically (Newton’s equation of motion):
    \[
    m_\alpha \ddot{\vec{r}}_\alpha = \vec{F}_\alpha
    \]
  - Forces on the ions are calculated by using the “Hellmann-Feynman theorem”:
    \[
    \vec{F}_\alpha(\vec{r}) = -\nabla_\alpha E[n(\vec{r})]
    \]
QMD simulations with VASP

VASP: Vienna Ab-Initio Simulation Package

Typical QMD flowchart
Accessible quantities in QMD simulations: Electronic, structural, optical properties, EOS …

- Each time step: $\vec{r}_i, \vec{v}_i, \vec{F}_i, \Psi_i$
- Full DFT calculation $\rightarrow$ Band structure, DOS
- Finite temperatures: $n(r) = \Sigma_i f(\varepsilon_i) |\Psi_i(r)|^2$ (Mermin)
- Calculation of $T$ and $p$ $\rightarrow$ EOS
- Average over hundreds of time steps: $g(r) \rightarrow S(k)$
- Autocorrelation function: self-diffusion coefficient via Einstein’s relation:
  \[
  D_s = \frac{1}{6t} \left\langle \left| \vec{r}_i(t) - \vec{r}_i(0) \right|^2 \right\rangle
  \]
  \[
  D_s = \frac{1}{3} \int_0^\infty dt \left\langle \vec{v}_i(t) \cdot \vec{v}_i(0) \right\rangle
  \]
Dynamic (optical) conductivity via QMD

• Dynamic conductivity \( \sigma(\omega) = \sigma_1(\omega) + i \sigma_2(\omega) \)

• via Kubo-Greenwood formula:

\[
\sigma_1(\omega) = \frac{2\pi e^2}{3m^2\Omega} \sum_k W(k) \sum_{i,j=1}^N \sum_{\alpha=1}^3 F_{ij} |D_{ij}|^2 \delta(\varepsilon_{j,k} - \varepsilon_{i,k} - \hbar\omega)
\]

\[
F_{ij} = \left[ f(\varepsilon_{i,k}) - f(\varepsilon_{j,k}) \right] / \omega , \quad |D_{ij}|^2 = \frac{1}{3} \sum_\alpha \left| \langle \Psi_{i,k} | \nabla_\alpha | \Psi_{j,k} \rangle \right|^2
\]

• Dielectric function:

\[
\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega) = 1 - \frac{1}{\varepsilon_0 \omega} \sigma_2(\omega) + i \frac{1}{\varepsilon_0 \omega} \sigma_1(\omega)
\]

• Kramers-Kronig relation:

\[
\sigma_2(\omega) = \frac{2}{\pi} \int P\left\{ \frac{\sigma_1(v)\omega}{(v^2 - \omega^2)} \right\}dv
\]

• Index of refraction:

\[
\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega) = \left[ n(\omega) + ik(\omega) \right]^2
\]

Thermal expansion of fluid metals (Hg, alkali metals Li-Cs) from the melting point up to the critical point:

Metal-to-nonmetal transition (localization of electrons)

Compression of molecular fluids (H₂, N₂, O₂, H₂O, CO₂) and noble gases (He, Ne, Ar, Kr, Xe) up to high pressure:

Nonmetal-to-metal transition (delocalization of electrons, band gap closure \(\rightarrow\) band gap problem!)

Test of the QMD method:

Comparison with accurate static high-pressure experiments and with dynamic shock wave experiments

Applications: QMD simulations for dense fluids and plasmas (WDM)
8A. Structure of expanded liquid metals

- Continuous phase transition by expanding the liquid thermally to the vapor phase around the critical point
- Pair correlation function determines the number of next neighbors, their distance, and the phase state

Slight change of the shape at the first and second peak can be interpreted as the occurrence of dimers and trimers ($\text{Rb}_2$, $\text{Rb}_3$) in liquid Rb at lower densities.

**QMD with VASP:**
32 to 64 atoms with 7 electrons per atom, canonical ensemble (Nosé-thermostat), 500-1000 time steps of 5-20 fs duration per run, 2-20 ps simulation time

Red circles: QMD data
Black line: Experimental data (Matsuda et al., 2006)
Contour plots of charge density in Rb

- Clustering: Rb$_2$, Rb$_3$
- Large voids
- Metal-nonmetal transition


373 K and 1.5 g/cm$^3$ near the melting point

2123 K and 0.59 g/cm$^3$ near the critical point
8B. Shock compressed fluid H

EOS of hydrogen: QMD compared with chemical picture – no PPT!

B. Holst, unpublished (2007)
Hugoniot curve for H from QMD

QMD results match all experimental data – except NOVA and chemical picture!

B. Holst, unpublished (2007)
8C. Electrical conductivity in dense He

8E. Phase diagram of warm dense water

M. French. See also T.R. Mattsson and M.P. Desjarlais, PRL 97, 017801 (2006)