Second Generation Car-Parrinello MD: Theory and Application to the Liquid/Vapor Interface

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Calculating Expectation Values from First Principles

The task of AIMD is to evaluate expectation values \( \langle O \rangle \) of arbitrary operators \( O(R_I, P_I) \) at finite temperature \( 1/\beta \) as accurate as possible

\[
\langle O \rangle = \frac{\int dR dP O(R_I, P_I) e^{-\beta E(R_I, P_I)}}{\int dR dP e^{-\beta E(R_I, P_I)}} = \lim_{t \to \infty} \frac{\sum O(R_I(t), P_I(t)) e^{-\beta E(R_I(t), P_I(t))}}{\sum e^{-\beta E(R_I(t), P_I(t))}}
\]

Opens the door to a variety of relevant static and dynamical properties

- The ions are treated classically (\( \rightarrow \) PIMC/PIMD)
- Accuracy of the potential energy surface
- Single particle finite size effects, although PBC helps a lot
- Statistical error, in particular due to correlation along a trajectory
- Large simulation cells (>> 100 atoms) are required
- Huge number of energy/force evaluations (>> 10^5) are essential
Calculating Expectation Values from First Principles

The task of AIMD is to evaluate expectation values $\langle \mathcal{O} \rangle$ of arbitrary operators $\mathcal{O}(\mathbf{R}_I, \mathbf{P}_I)$ at finite temperature $1/\beta$ as accurate as possible.

$$
\langle \mathcal{O} \rangle = \frac{\int d\mathbf{r} d\mathbf{p} \, \mathcal{O}(\mathbf{R}_I, \mathbf{P}_I) e^{-\beta E(\mathbf{R}_I, \mathbf{P}_I)}}{\int d\mathbf{r} d\mathbf{p} \, e^{-\beta E(\mathbf{R}_I, \mathbf{P}_I)}} = \lim_{t \to \infty} \frac{\sum \mathcal{O}(\mathbf{R}_I(t), \mathbf{P}_I(t)) e^{-\beta E(\mathbf{R}_I(t), \mathbf{P}_I(t))}}{\sum e^{-\beta E(\mathbf{R}_I(t), \mathbf{P}_I(t))}}
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A very brief review of CPMD I

The CP Lagrangian

\[ \mathcal{L}_{\text{CP}}(\{\psi_i\}; R_I, \dot{R}_I) = \frac{1}{2} \mu \sum_{i=1}^{M} \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \frac{1}{2} \sum_{I=1}^{N} M_I \dot{R}_I^2 - E[\{\psi_i\}; R_I] + \sum_{i,j} \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}) \]

- \( \psi_i(r, t) \) are thought of classical fields
- Ions and \( e^- \) are on the same footing
- Fictitious mass parameter \( \mu \)
- \( E[\{\psi_i\}; R_I] \) vs. \( \min E[\{\psi_i\}; R_I] \)

\[
\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{R}_I} = \frac{\partial \mathcal{L}}{\partial R_I} \\
\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \langle \dot{\psi}_i \rangle} = \frac{\partial \mathcal{L}}{\partial \langle \psi_i \rangle}
\]
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\[ - E[\{\psi_i\}; R_I] + \sum_{i,j} \Lambda_{ij}(\langle \psi_i | \psi_j \rangle - \delta_{ij}) \]

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A very brief review of CPMD II

The Equations of Motion

\[ M_I \ddot{R}_I = -\nabla_{R_I} \left[ E[\{\psi_i\}; R_I] \right] \begin{bmatrix} \langle \psi_i | \psi_j \rangle = \delta_{ij} \end{bmatrix} \]

\[ = -\frac{\partial E}{\partial R_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial R_I} \langle \psi_i | \psi_j \rangle \]

\[ \mu \ddot{\psi}_i(r, t) = -\frac{\delta E}{\delta \langle \psi_i \rangle} + \sum_j \Lambda_{ij} |\psi_j\rangle \]

\[ = -\hat{H}_e \langle \psi_i \rangle + \sum_j \Lambda_{ij} |\psi_j\rangle \]

- If \( \mu \) is sufficiently small, the electrons adiabatically follow the ions
- In this case the metastable state can be sustained and \( \ddot{\psi}_i \approx 0 \)
- Energies & Forces are NOT on the BO surface, but are consistent
A very brief review of CPMD III
The fictitious mass parameter $\mu$

Principal task of $\mu$: Coupling between $\dot{R}_I$ and $\dot{\psi}_i$

$$|\psi_\mu(r, t) - \psi_0(r, t)| \leq C\sqrt{\mu}$$

$$\Delta t_{\text{max}} \propto \sqrt{\frac{\mu}{\Delta E_{\text{gap}}}}$$

- $\mu$ acts as a continuous slider between speed and accuracy
- Typically, the timestep is $\sim 5 \times 10^{-10}$ smaller than in BOMD
- Depends on the application if either CPMD or BOMD is to favor
- Metals are problematic: Finite electron temperature or thermostats

Desirable to eliminate $\mu$!
A very brief review of CPMD III
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Car-Parrinello vs. Born-Oppenheimer Dynamics

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<thead>
<tr>
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<th>CPMD</th>
<th>BOMD</th>
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<tbody>
<tr>
<td>Preservation of the Conserved Quantity:</td>
<td>excellent</td>
<td>reasonable</td>
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<tr>
<td>Iterative Wavefunction Optimization:</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Integration Time-Step:</td>
<td>small</td>
<td>large</td>
</tr>
<tr>
<td>Exactly on the BO-Surface:</td>
<td>slightly above</td>
<td>yes</td>
</tr>
<tr>
<td>Systems with Small Bandgap:</td>
<td>difficult</td>
<td>possible</td>
</tr>
</tbody>
</table>

- **Goal:** Unify the best of CPMD & BOMD
  - **Stability:** CP-like propagation of the electronic degrees of freedom
  - **Efficiency:** Large integration time steps, without SCF-cycle
  - **Accuracy:** Dynamics essentially indistinguishable from BOMD
  - **Error Control:** Adaptive control of the deviation from the BO-surface
  - **Robustness:** Systems with vanishing band-gap can be treated
The Equations of Motion

\[ M_I \ddot{R}_I = -\nabla_{R_I} \left[ \min_{\{\psi_i\}} E[\{\psi_i\}; R_I] \right] \left\{ \langle \psi_i | \psi_j \rangle = \delta_{ij} \right\} \]

\[ = -\frac{\partial E}{\partial R_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial R_I} \langle \psi_i | \psi_j \rangle \]

\[ - 2 \sum_i \frac{\partial \langle \psi_i |}{\partial R_I} \left[ \frac{\partial E_{\text{NSC}}}{\partial \langle \psi_i |} - \sum_j \Lambda_{ij} | \psi_j \rangle \right] \]
The Equations of Motion

The Coupled Electron-Ion Molecular Dynamics II


\[ \mu \frac{d^2}{dt^2} |\psi_i(r, t)\rangle + \gamma \frac{d}{dt} |\psi_i(r, t)\rangle + \hat{H}_{KS} |\psi_i(r, t)\rangle - \sum_j \Lambda_{ij} |\psi_j(r, t)\rangle = 0 \]

\[ \frac{\mu}{\vartheta_c^2} \frac{d^2}{d\tau^2} |\psi_i(r, \tau)\rangle + \frac{\gamma}{\vartheta_c} \frac{d}{d\tau} |\psi_i(r, \tau)\rangle = -\hat{H}_{KS} |\psi_i(r, \tau)\rangle + \sum_j \Lambda_{ij} |\psi_j(r, \tau)\rangle \]

\[ t = \tau \vartheta_c \quad \& \quad \vartheta_c = \sqrt{\mu} = \frac{1}{\omega} \]

\[ \frac{d^2}{d\tau^2} |\psi_i(r, \tau)\rangle + \gamma \omega \frac{d}{d\tau} |\psi_i(r, \tau)\rangle = -\hat{H}_{KS} |\psi_i(r, \tau)\rangle + \sum_j \Lambda_{ij} |\psi_j(r, \tau)\rangle \]
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\[ \frac{d^2}{d\tau^2} |\psi_i (r, \tau) \rangle = -\frac{\delta E_{\text{NSC}}}{\delta \langle \psi_i |} - 2\zeta \frac{d}{d\tau} |\psi_i (r, \tau) \rangle + \sum_j \Lambda_{ij} |\psi_j (r, \tau) \rangle \]

\[ 2\zeta \overset{\text{def}}{=} \frac{\gamma}{\mu \omega} = \gamma \omega \]
The Always Stable Predictor Corrector (ASPC) Method

Propagating the electrons by a Gear-type predictor-corrector integrator (Kolafa, JCC 04)

- Instead of $C$ the contra-covariant density matrix $PS$ is propagated
- As $PS$ is an approximate projector onto the occupied subspace:

$$C^p(t_n) \approx \sum_{m=1}^{K} (-1)^{m+1} m \frac{2K}{K-m} \frac{2K-2}{K-1} C(t_{n-m})C^T(t_{n-m}) \times S(t_{n-m})C(t_{n-1})$$

- The corrector consists of one preconditioned gradient calculation
  Neither diagonalization nor iterative minimization is required!
- For a certain choice of $\alpha$ "always stability" can be proven
- The corrector can be iteratively applied, to control the deviation

$$C(t_n) = \alpha \text{MIN} [C^p(t_n)] + (1 - \alpha) C^p(t_n) ,$$

with $\alpha = \frac{K}{2K-1}$
Orbital Transformations as a Corrector


\[ C(X) = C^p(t_n) \cos(U) + XU^{-1} \sin(U), \text{with } U = \left( X^T S X \right)^{1/2} \]

The variable \( X \) has to obey the linear constraint \( X^T S C^p(t_n) = 0 \)

\[
\frac{\partial}{\partial X} \left( E[C(X)] + Tr[X^T S C^p \Lambda] \right) = \frac{\partial E[C(X)]}{\partial C} \frac{\partial C(X)}{\partial X} + S C^p \Lambda,
\]

where \( \Lambda = -[(S C^p)^T S C^p]^{-1} (S C^p)^T \frac{\partial E[C(X)]}{\partial X} \)

- The orthonormalization constraint is fulfilled by construction
- The requirements of a SCF solution and exact eigenfunctions are both fully bypassed
- The non-self-consistent energy functional is solely evaluated: Neither diagonalization nor iterative minimization is required!
The Harris-Foulkes Functional

\[ E_{PC}[\rho^p] = Tr \left[ C^T H[\rho^p] C \right] - \frac{1}{2} \int dr \int dr' \frac{\rho^p(r) \rho^p(r')}{|r - r'|} \]

\[ - \int dr \ V_{XC}[\rho^p] \rho^p + E_{XC}[\rho^p] + E_{II} , \]

- Linear partial differential equation, since it depends only on \( \rho^p \)
- Can be solved non-self-consistently
- Converges to the KS-equation at self-consistency, with \( \rho^p \rightarrow \rho^{SC} \)
- Not variational, but stationary at the ground state
- Typically a better ground-state estimate than the KS-equation
- The error in the energy is \( O((\Delta \rho)^2) \) and 1st order for the forces
- However, as \( \Delta \rho \neq 0 \) an extra term in the force calculation appears

\[ - \int dr \ \left\{ \left[ \frac{\partial V_{XC}[\rho^p]}{\partial \rho^p} \right] \Delta \rho + V_H[\Delta \rho] \right\} (\nabla I \rho^p) \]
The Main Conceptual Ideas


- BOMD allows for large timesteps, but incomplete wavefunction minimization leads to more or less pronounced sampling errors
- It is sufficient to approach the BO-surface by design of a CEIMD CP-like BOMD, to fully bypass the SCF-cycle and iterative minimization by correcting for sampling errors
- It can be advantageous to treat the nuclear and electronic degrees of freedom NOT on the same footing
- For the short-term integration of the electrons accuracy is crucial
- This should telling us something: Don’t use the same integrators!
- Thus the explicit, but non-symplectic ASPC integrator is used
- Non-symplectic integrators generally turn a conservative system into a dissipative one, leading to an exponential decay in energy
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The Modified Langevin Equation

\[
M_I \ddot{R}_I = F_I^{BO} - M_I \dot{R}_I (\gamma_D + \gamma_L) + (\Xi^D_I + \Xi^L_I) \\
= F_I^{PC} - \gamma_L M_I \dot{R}_I + (\Xi^D_I + \Xi^L_I)
\]

To guarantee an accurate sampling of the Boltzmann distribution, the noise has to obey the fluctuation dissipation theorem:
\[
\langle \{\Xi^D_I(0) + \Xi^L_I(0)\} \{\Xi^D_I(t) + \Xi^L_I(t)\} \rangle = 2(\gamma_D + \gamma_L)M_I k_B T \delta(t)
\]

If the dissipation is indeed exponential decaying, we can do the substitution and still get a rigorously defined canonical ensemble \(\gamma_D\), such that the equipartition theorem \(\left\langle \frac{1}{2} M_I \dot{R}_I^2 \right\rangle = \frac{3}{2} k_B T\) holds.

To integrate the equations of motion under Brownian motion, the algorithm of Vanden-Eijnden & Ciccotti is used.

The white noise condition is satisfied by definition.
Is our assumption justified?
Is the Kinetic Energy Distribution Maxwell distributed?

- Si$_{64}$ (lq)
- 3000 K
- 3D PBC
- LDA
- GTH-PP
- DZVP
- 100 Ry
- $t > 1$ ns

A correct canonical sampling of the Boltzmann distribution is performed!
Is our assumption justified?
Is the Kinetic Energy Distribution Maxwell distributed?

Si\textsubscript{64} (lq)
3000 K
3D PBC
LDA
GTH-PP
DZVP
100 Ry
t > 1 ns

A correct canonical sampling of the Botzmann distribution is performed!
24 SiO$_2$ (lq) at 3500 K
A DZVP basis set, 280 Ry density cutoff and t = 1.0 fs are used
Constantly bonds are swiftly broken and formed
Worst case scenario, as the density matrix is rapidly varying
Results in terms of accuracy

Deviations from the Born-Oppenheimer Surface

Deviations from the Born-Oppenheimer Surface II

Energy [Hartree]:
-865.4
-865.2
-865.0
-864.8

Mean force deviation [a.u.]:
-0.0002
-0.0001
0
0.0001
0.0002

Time [fs]:
0 200 400 600 800 1000

BOMD reference
1 corrector step

Instantaneous mean force deviation
Average mean force deviation

Next Generation CPMD: Theory & Application
NAMET Workshop, 23.09.2010

Thomas D. Kühne (University of Mainz)
The energy shift is reasonable small and importantly constant

Energy differences are very well reproduced

The electrons are solely propagated: No SCF cycle at all

The deviation from the BO surface is systematically controllable
Results in terms of accuracy
Static and dynamic properties

Partial Pair-Correlation Functions

For these systems a speed-up of two orders of magnitude is observed.

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Literature

- \( \text{Ge}_2 \text{Sb}_2 \text{Te}_5 \)

- \( \text{TeO}_2 \)

- \( \text{SiO}_2 \)

- LiAl

- \( \text{Sb}_2 \text{Te}_3 \)

Large-scale efficient Langevin dynamics, and why it works
Partial Pair-Correlation Function: Finite Size Effects

Partial Pair-Correlation Function: XC Functionals

Translational Self-Diffusion for Bulk Water

Finite-size effects, extrapolation to infinity and the shear viscosity

- $D_{128}^{BO} = 0.059(6) \ \AA^2 / \text{ps}$
- $D_{128}^{CP} = 0.060(1) \ \AA^2 / \text{ps}$
- $D_\infty = D_{\text{PBC}} + \frac{k_B T \zeta}{6\pi \eta L}$
- $D_\infty^{CP} = 0.0789 \ \AA^2 / \text{ps}$
- $D_{\text{Exp.}} = 0.2395 \ \AA^2 / \text{ps}$
- Shear viscosity:
  - $\eta^{CP} = 21.22 \times 10^{-4} \ \frac{\text{kg}}{\text{ms}}$
  - $\eta_{\text{Exp.}} = 8.92 \times 10^{-4} \ \frac{\text{kg}}{\text{ms}}$

- Diffusion is better reproduced by DFT than generally appreciated
- Translational shear viscosity is much less system size dependent
- System sizes to converge $D_{\text{PBC}}$ are essentially out of reach
Hydrogen Bond Network Structure

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<thead>
<tr>
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Velocity Autocorrelation and Power Spectrum
The Anharmonic Vibrational Density of States
Spatial Distribution Function

At the DFT level of accuracy liquid water is tetrahedral coordinated!
At the DFT level of accuracy liquid water is tetrahedral coordinated!
Computational Details

- CP2K/QUICKSTEP (cp2k.berlios.de)
- Orthorombic box \((15.66 \, \text{Å} \times 15.66 \, \text{Å} \times 55.00 \, \text{Å})\) consisting of 384 light water molecules
- 2D PBC using the decoupling scheme of P. Blöchl
- Temperature very close to 300 K and \(\Delta t = 0.5 \, \text{fs}\)
- Semilocal BLYP GGA XC functional
- Empirical (damped \(C_6/R^6\)) vdW correction
- In total more than 300 ps of simulation time
- Molecular optimized TZV2P Gaussian basis set
- BSSE \(\approx 0.3 \, \text{kcal/mol}\) with a std \(\leq 0.01 \, \text{kcal/mol}\)
- GTH-PP along with a density cutoff of 320 Ry
- \(K = 7 \Rightarrow \text{time reversibility up to } \mathcal{O}(\Delta t^{12})\)
- \(\gamma_D = 8.65 \times 10^{-5} \, \text{fs}^{-1}\) and \(\gamma_L = 1.35 \times 10^{-5} \, \text{fs}^{-1}\)
Hydrogen Bond Definition via the 2D PMF

Defining the Surface: Density Profile

\[ \rho(z) = a \left\{ 1 + \tanh \left[ b(z - c) \right] \right\} \rightarrow \text{GDS at } c = 44.5 \text{ Å} \pm 2.5 \text{ Å} \]

VdW correction systematically improves the density of liquid water
Hydrogen Bonding at the Liquid-Vapor Interface

<table>
<thead>
<tr>
<th></th>
<th>2D PMF W(R, $\beta$)</th>
<th>2D PMF W(r, $\theta$)</th>
<th>Kuo &amp; Mundy Science 05</th>
<th>Experiment SFG (Chen)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>bulk</td>
<td>surf.</td>
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<tr>
<td>DD</td>
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<tr>
<td>SD</td>
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<td>45%</td>
<td>15%</td>
<td>45%</td>
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<tr>
<td>ND</td>
<td>1%</td>
<td>6%</td>
<td>1%</td>
<td>7%</td>
</tr>
<tr>
<td>free HB</td>
<td>8%</td>
<td>29%</td>
<td>8%</td>
<td>29%</td>
</tr>
<tr>
<td>mean HB</td>
<td>3.7</td>
<td>2.9</td>
<td>3.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

- Very recently Saykally et al. have revisited their own TIY-EXAFS experiments and found that the occurrence of SD and ND are substantially lower than initially reported back in 2001/2002.
- Most of the discrepancy can be explained by the HB definition...
Liquid-Vapor Interface

Hydrogen Bonding at the Liquid-Vapor Interface

<table>
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<tr>
<th></th>
<th>2D PMF $W(R, \beta)$</th>
<th>2D PMF $W(r, \theta)$</th>
<th>Kuo &amp; Mundy Science 05</th>
<th>Experiment SFG (Chen)</th>
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<td>bulk</td>
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<tr>
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<td>45%</td>
</tr>
<tr>
<td>ND</td>
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Most of the discrepancy can be explained by the HB definition
Surface Relaxation
Comparing the distribution of OH-vectors and lone pair orbitals:
- OH bonds prefer to protrude out of the water phase
- However, the lone pair orbitals tend to point into the water phase
- Consistent with the conjecture that the order of Layer I is to maximize the HB and to minimize the exposed partial charge
Orientational Distribution near the Surface: Layer II


- Only Layer I and II obeys structural order
- The OH vectors of Layer I is peaked at $0^0$ and at around $107^0$, i.e. tends to donate HB’s to Layer II
- In Layer II the opposite is the case - the OH bonds prefer to point into the bulk phase, while providing lone pair orbitals to Layer I
Acknowledgements

Thanks for your attention!