



PRAGUE INSTITUTE OF CHEMICAL TECHNOLOGY

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Molecular dynamics simulations of polarizable molecules

Gear-like formalism of the Always Stable Predictor-Corrector method

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The electrostatic field in systems with induced dipoles (multipoles) is not given explicitly but by an implicit equation for a self-consistent field (SCF). In molecular dynamics (MD) simulations, an approximation of the SCF must be known at every integration step and therefore any lengthy solving of this equation should be avoided.

In this paper, criteria for a high-quality integration method are summarized. Available methods are reviewed and compared. The new result of this contribution is derivation an equivalent formulation of the recently extended Always Stable Predictor-Corrector (ASPC) method¹ in the form of the Gear predictor-corrector scheme. There is no gain in accuracy or efficiency, but this formulation may simplify implementation provided that the Gear method is already used to integrate the coordinates.

MD of polarizable systems

The Newton equations of motion

$$\ddot{\mathbf{r}}_i = \frac{1}{m_i} \mathbf{f}_i(\mathbf{r}_1, \dots, \mathbf{r}_N; \boldsymbol{\mu}_1, \dots, \boldsymbol{\mu}_N) \quad (1)$$

are to be numerically integrated.

Induced dipoles $\boldsymbol{\mu}_i$ in (1) are given by the **implicit equation**

$$\boldsymbol{\mu}_i = \boldsymbol{\alpha}_i \cdot \mathbf{E}_i(\boldsymbol{\mu}_1, \dots, \boldsymbol{\mu}_N; \mathbf{r}_1, \dots, \mathbf{r}_N) \equiv \mathbf{M}_i(\boldsymbol{\mu}_1, \dots, \boldsymbol{\mu}_N), \quad (2)$$

where $\boldsymbol{\alpha}_i$ is polarizability (generally tensor) and \mathbf{E}_i is electrostatic field on particle (i).

The fixed point of (2) is the **self-consistent field** (SCF):

$$\boldsymbol{\mu}_i = \mathbf{M}_i(\boldsymbol{\mu}_1, \dots, \boldsymbol{\mu}_N), \quad \text{concisely: } \boldsymbol{\mu} = \mathbf{M}(\boldsymbol{\mu}).$$

Criteria of a good method

- Efficiency: one evaluation of forces and field per integration step
less than 1 does not make sense because forces have to be calculated anyway
more than 1 is inefficient
- Sufficient accuracy of induced dipoles
- Good energy conservation
- Easy implementation

Available methods

PI: Predicted Iterations, iterations² optimized by prediction and relaxation³
● accurate but expensive (many calculations of forces/MD step)

CP: Car-Parrinello-like method (extended Lagrangian) uses extra dynamic variables (“charges on springs”) mimicking mechanically the induced dipoles^{4,5}

Do not confuse with quantum Car-Parrinello MD

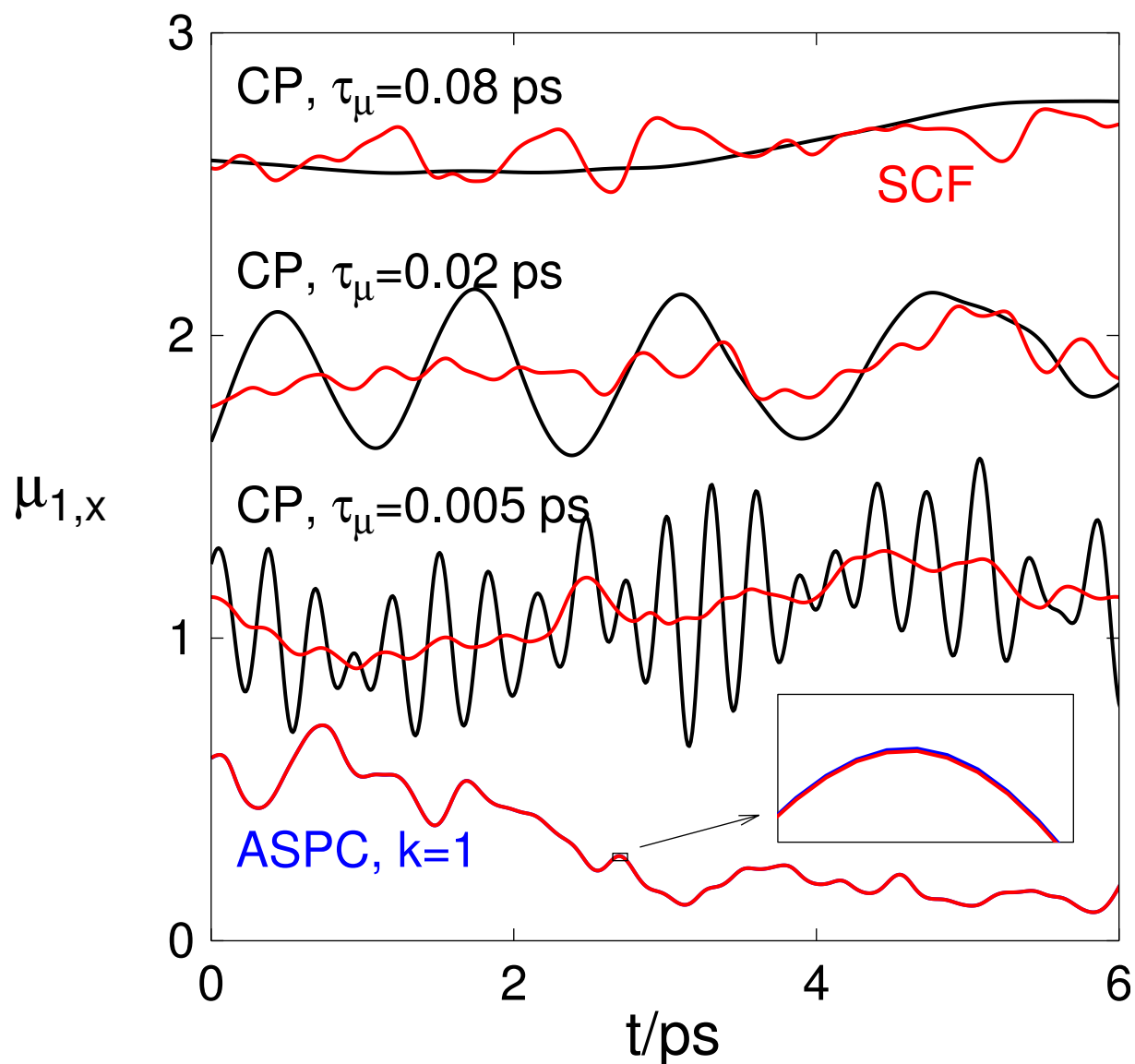
● fast (1 calculation of forces/MD step) but inaccurate

CP (T=0): CP + dipole subsystem at very low T + multiple timestep MD⁶
● accurate and fast but complicated

ASPC Always Stable Predictor-Corrector combines a special predictor and relaxation¹

● accurate, fast, and simple (the method, not its derivation)

Comparison of methods



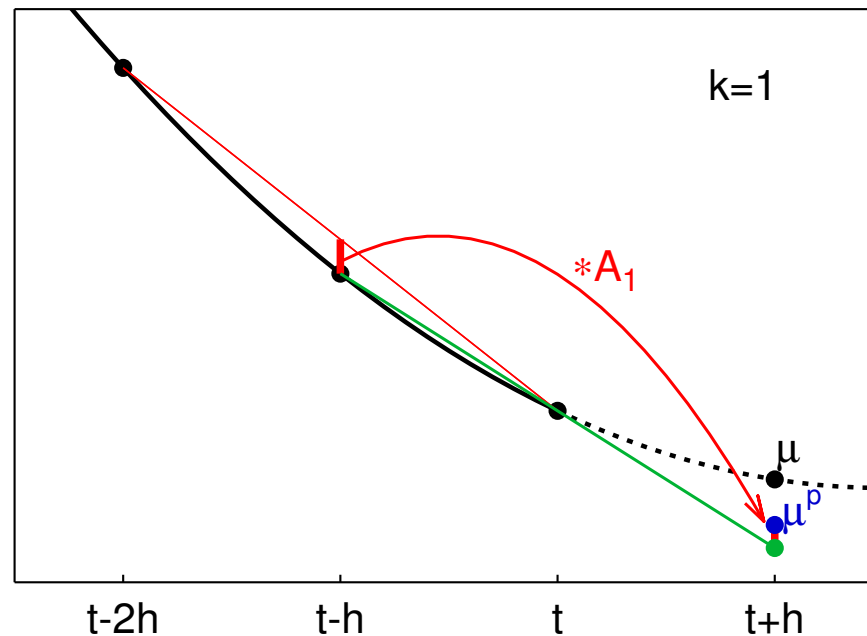
Time development of a selected induced dipole in polarizable TIP4P water³

ASPC theory

The modified linear **predictor** (local order $\mathcal{O}(h^2)$)

$$\begin{aligned} \mu^p(t+h) &= 2\mu(t) - \mu(t-h) \\ &+ \sum_{j=1}^k A_j \left\{ \mu(t - [j+1]h) - 2\mu(t - jh) + \mu(t - [j-1]h) \right\} \end{aligned} \quad (3)$$

$$= B_1\mu(t) + B_2\mu(t-h) + B_3\mu(t-2h) + \dots \quad (4)$$



The **corrector** consists of one iteration with relaxation (mixing, damping):

$$\mu(t+h) = \omega M(\mu^p) + (1-\omega)\mu^p. \quad (5)$$

How to determine B_1, \dots, B_{k+1} : Time reversibility

Time reversibility = long time energy conservation

Let us Taylor-expand (4). The error of the predictor (i.e., rhs – lhs) is

$$\sum_{l=0}^{\infty} \frac{(-h)^l}{l!} C_l \mu^{(l)}(t), \quad (6)$$

where

$$C_l = \sum_{j=0}^{k+1} B_{j+1} j^l.$$

The terms at even powers of h in (6) are time reversible, the odd terms cause time irreversibility seen as energy drift.

We are looking for a method with vanishing coefficients at odd powers of h .

From (3) it follows that $C_0 = C_1 = 0$.

Predictor: $O(h^{2k+1})$ time-reversible solution

After some algebra one can derive

$$\begin{aligned} B_1 &= 1(4k+6)\frac{1}{(k+3)}, \\ B_2 &= -2(4k+6)\frac{(k+1)}{(k+3)(k+4)}, \\ B_3 &= 3(4k+6)\frac{(k+1)(k+0)}{(k+3)(k+4)(k+5)}, \\ B_4 &= -4(4k+6)\frac{(k+1)(k+0)(k-1)}{(k+3)(k+4)(k+5)(k+6)}, \\ &\vdots \\ B_i &= 0 \text{ for } i > k+2. \end{aligned} \tag{7}$$

For instance, for $k=1$ it holds $C_0 = C_1 = C_3 = 0$, $C_2 \neq 0$.

How to determine ω : Stability

Stability = errors do not cumulate

Let us study the “primitive” right-hand side:

$$M(\mu) = \lambda\mu \quad (\text{SCF: } \mu = 0),$$

where λ represents the biggest eigenvalue of linearized operator M (rate of convergence of direct iterations),

Analogy: $y^{(n)} = \lambda y$ for ordinary differential equations.

and let us start with nonzero $\mu(t), \mu(t-h), \dots$

We need an *always stable* method,
i.e., $\lim_{t \rightarrow \infty} \mu(t) = 0$ for all $|\lambda| < 1$.

Mathematically: All roots of the characteristic equation of the recurrence for error propagation are less than 1.

Solution: The corrector (5) is always stable for¹

$$\omega = \frac{k+2}{2k+3}. \quad (8)$$

ACSP summary

Coefficients of the ASPC method, (7), and the (unoptimized) relaxation parameter ω , (8).

k	time rev.	B_1	B_2	B_3	B_4	B_5	B_6	ω
0	$\mathcal{O}(h^3)$	2	-1					2/3
1	$\mathcal{O}(h^5)$	2.5	-2	0.5				0.6
2	$\mathcal{O}(h^7)$	2.8	-2.8	1.2	-0.2			4/7
3	$\mathcal{O}(h^9)$	3	-24/7	27/14	-4/7	1/14		5/9
4	$\mathcal{O}(h^{11})$	22/7	-55/14	55/21	-22/21	5/21	-1/42	6/11

The above values of ω guarantee stability for any (converging) SCF. In practice $\lambda \in (\lambda_{\min}, \lambda_{\max}) \subset (-1, 1)$ and larger ω can be used which increases accuracy but requires some preliminary MD runs with given system.

ASPC, $k = 2$, is recommended as a compromise between complexity and good time reversibility.

Gear formulation—version 1

Instead of the history (4), let us have a vector of derivatives at time t :

$$\mathbf{H}(t) = \begin{pmatrix} \boldsymbol{\mu}(t) \\ \boldsymbol{\mu}(t-h) \\ \vdots \\ \boldsymbol{\mu}(t-h[k+1]) \end{pmatrix} \longrightarrow \mathbf{R}(t) = \begin{pmatrix} \boldsymbol{\mu}(t) \\ h\dot{\boldsymbol{\mu}}(t) \\ \frac{h^2}{2}\ddot{\boldsymbol{\mu}}(t) \\ \vdots \end{pmatrix} \equiv \begin{pmatrix} R_0(t) \\ R_1(t) \\ R_2(t) \\ \vdots \end{pmatrix}. \quad (9)$$

These two representations are equivalent: the Taylor expansion of the interpolation polynomial of $\mathbf{H}(t)$ is $\mathbf{R}(t)$. In the opposite direction, the values calculated from \mathbf{R} for $t, t-h, \dots$, give the history:

$$\begin{aligned} \boldsymbol{\mu}(t) &= R_0(t) \\ \boldsymbol{\mu}(t-h) &= R_0(t) - R_1(t) + R_2(t) - R_3(t) + \dots \\ \boldsymbol{\mu}(t-2h) &= R_0(t) - 2R_1(t) + 4R_2(t) - 8R_3(t) + \dots \\ \boldsymbol{\mu}(t-3h) &= R_0(t) - 3R_1(t) + 9R_2(t) - 27R_3(t) + \dots \\ &\vdots \end{aligned}$$

These equations can be written in the matrix form:

$$\mathbf{H}(t) = \mathbf{T} \cdot \mathbf{R}(t),$$

where

$$\mathbf{T} = \begin{pmatrix} 1 & & & & \\ 1 & -1 & 1 & -1 & \dots \\ 1 & -2 & 4 & -8 & \dots \\ 1 & -3 & 9 & -27 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

The predictor for $\mathbf{H}(t)$ is

$$\mathbf{H}^p(t+h) = \mathbf{P} \cdot \mathbf{H}(t),$$

where

$$\mathbf{P} = \begin{pmatrix} B_1 & B_2 & B_3 & B_4 & \dots \\ 1 & & & & \\ & 1 & & & \\ & & 1 & & \\ & & & \dots & \end{pmatrix}$$

The first row of \mathbf{P} is (4), the off-diagonal of 1s represents the $t \rightarrow t + h$ shift.

Combination of the above matrices gives the predicted \mathbf{R} :

$$\mathbf{R}^p(t + h) = \mathbf{G} \cdot \mathbf{R}(t),$$

where

$$\mathbf{G} = \mathbf{T}^{-1} \cdot \mathbf{P} \cdot \mathbf{T}. \quad (10)$$

The corrector (5) applies to the first element of vector \mathbf{H}^p and after the above transformation it can be written in the matrix form

$$\mathbf{R} = \mathbf{R}^p + \omega e \mathbf{C}, \quad (11)$$

where

$$e = M(\mathbf{R}_0^p) - \mathbf{R}^p \equiv M(\mu^p) - \mu_P \quad (12)$$

is a one-step error in induced dipoles and \mathbf{C} denotes the first column of matrix \mathbf{T}^{-1} .

Note that rows are numbered from 0 while columns from 1.

Several first predictors and correctors:

$k = 0:$

1	1	1
	1	1

Key:

<i>G</i>	<i>C</i>
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$k = 1:$

1	1		1
	1	0.5	1.5
		0.5	0.5

$k = 2:$

1	1	0.2	-1.4	1
	1	8/15	-1.4	11/6
		0.2	0.6	1
		-2/15	0.6	1/6

(recommended)

$k = 3:$

1	1	2/7	-8/7	-4/7	1
	1	43/84	-41/28	61/84	25/12
		-1/24	-1/8	89/24	35/24
		-25/84	3/28	281/84	5/12
		-5/168	-5/56	157/168	1/24

Gear formulation—version 2

If we do not demand the particular form of \mathbf{R} with higher derivatives, (9), the Gear-like method is not unique. E.g., with derivatives replaced by differences one gets

$$\mathbf{R}(t) = \begin{pmatrix} \mu(t) \\ \mu(t) - \mu(t-h) \\ \frac{1}{2!}[\mu(t) - 2\mu(t-h) + \mu(t-2h)] \\ \frac{1}{3!}[\mu(t) - 3\mu(t-h) + 3\mu(t-2h) - \mu(t-3h)] \\ \vdots \end{pmatrix}. \quad (13)$$

Here both \mathbf{T} and \mathbf{T}^{-1} are known explicitly:

$$\mathbf{T}^{-1} = \begin{pmatrix} 1 \\ 1 & -1 \\ \frac{1}{2!} & -\frac{2}{2!} & \frac{1}{2!} \\ \frac{1}{3!} & -\frac{3}{3!} & \frac{3}{3!} & -\frac{1}{3!} \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad \mathbf{T} = \begin{pmatrix} 1 \\ 1 & -1 \\ 1 & -2 & 2! \cdot 1 \\ 1 & -3 & 2! \cdot 3 & 3! \cdot 1 \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

Again, (10), (11), and (12) apply.

Several first predictors and correctors for version 2:

$k = 0$:

1	1	1
	1	1

Key:

<i>G</i>	<i>C</i>
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$k = 1$:

1	1	1	1
	1	1	1
		0.5	0.5

$k = 2$:

1	1	1.2	1.2	1
	1	1.2	1.2	1
		0.6	0.6	0.5
		-2/15	0.2	1/6

(recommended)

$k = 3$:

1	1	9/7	12/7	12/7	1
	1	9/7	12/7	12/7	1
		9/14	6/7	6/7	1/2
		-5/42	2/7	2/7	1/6
		-5/168	-5/28	1/4	1/24

Algorithm—history version

The algorithm for one step of the Verlet method with ASPC in the standard version (4) and (5).

Notation: r is shorthand for (r_1, \dots, r_N) at time t (implemented typically as an array of vectors) while $r_1 = r(t - h)$, $\mu_1 = \mu(t - h)$, etc.

- $\mu^p := 2.8\mu_1 - 2.8\mu_2 + 1.2\mu_3 - 0.2\mu_4$ // induced dipole predictor ($k = 2$)
- $E := \text{Elst}(r, \mu^p)$ // electrostatic field
- $f := \text{force}(r, E)$ // the force (usually E and f calculations are merged)
- $r_{\text{next}} := 2r - r_1 + h^2 \frac{f}{m}$ // Verlet: $r_{\text{next}} = r(t + h)$; SHAKE may follow
- $\mu := \omega\alpha \cdot E + (1 - \omega)\mu^p$ // dipole corrector, $\mu = \mu(t)$
- $t := t + h$
- $\mu_4 := \mu_3; \mu_3 := \mu_2; \mu_2 := \mu_1; \mu_1 := \mu$; // time shift: dipoles
- $r_1 := r; r := r_{\text{next}}$ // time shift: coordinates

Algorithm—Gear versions

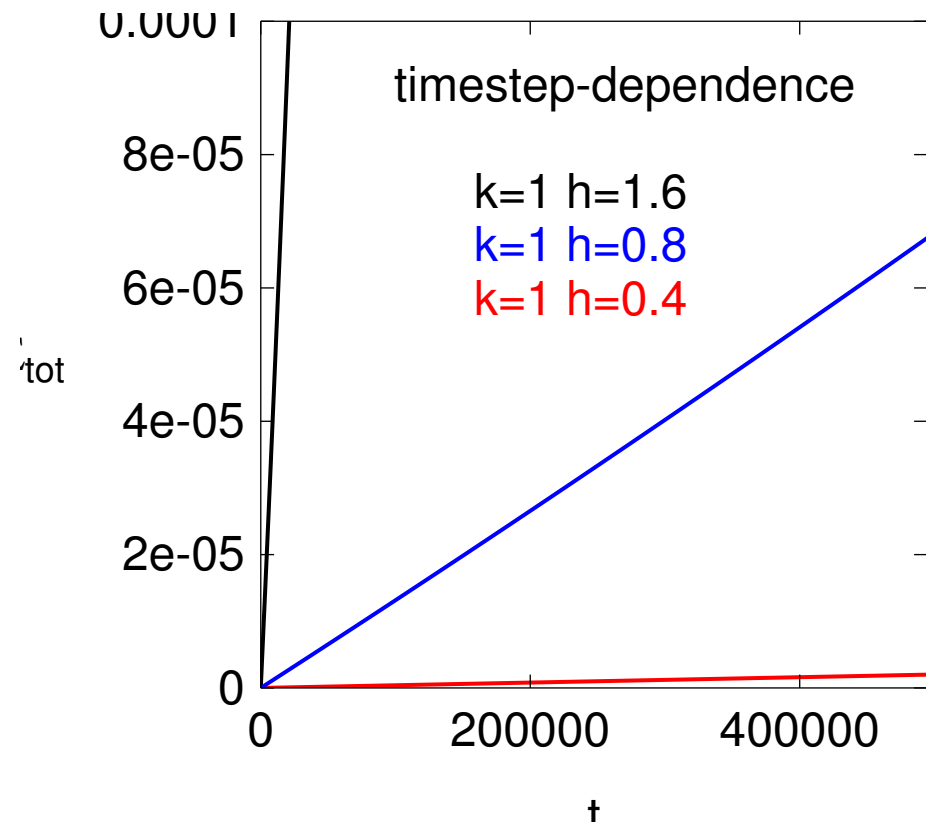
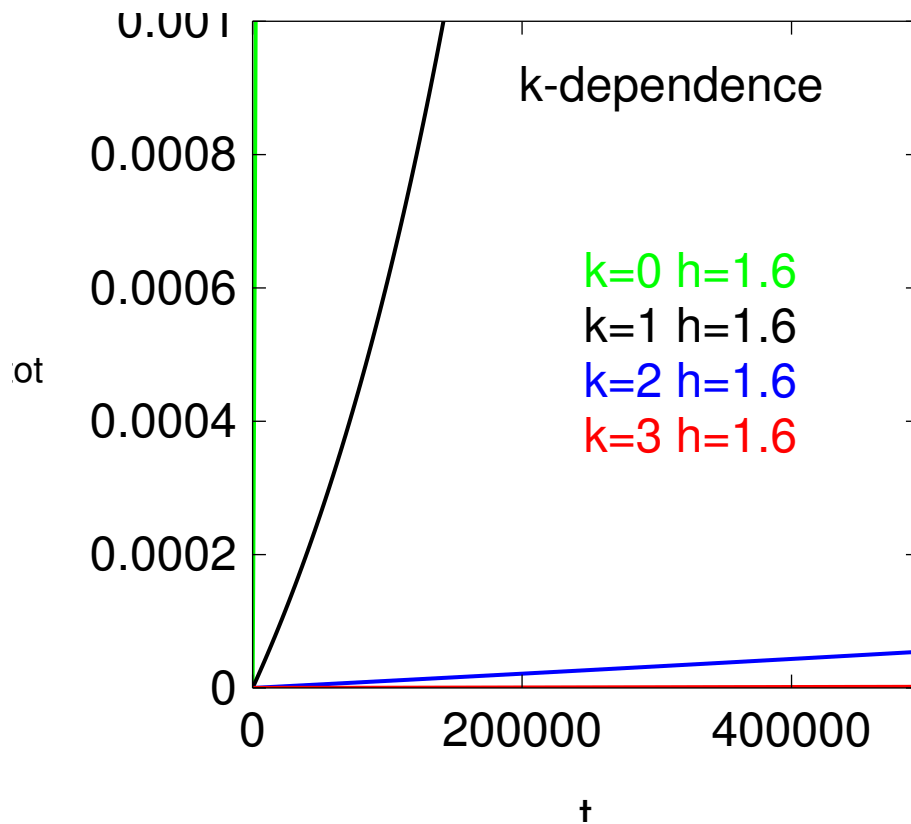
The algorithm for both MD and ASCP in the Gear formulation. Three-value Gear method (equivalent to Verlet) is recommended with the predictor

matrix $\mathbf{G}_r = \begin{pmatrix} 1 & 1 & 1 \\ 0 & 1 & 2 \\ 0 & 0 & 1 \end{pmatrix}$ and the corrector vector $\mathbf{C}_r = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$.

- $\mathbf{R}^p := \mathbf{G} \cdot \mathbf{R}$ // predictor for dipoles
- $\mathbf{R}_r^p := \mathbf{G}_r \cdot \mathbf{R}_r$ // predictor for coordinates, $\mathbf{R}_r = \begin{pmatrix} r \\ h\dot{r} \\ \frac{h^2}{2}\ddot{r} \\ \vdots \end{pmatrix}$
- $E := \text{Elst}(\mathbf{R}_{r,0}^p, \mu^p)$ // electrostatic field
- $f := \text{force}(\mathbf{R}_{r,0}^p, E)$ // the force
- $e := \alpha \cdot E - \mathbf{R}_0^p$ // error of the predictor for dipoles
- $\mathbf{R} := \mathbf{R}^p + \omega e \mathbf{C}$ // corrector for dipoles, $\mathbf{R}_0 = \mu(t + h)$
- $e_r := \frac{h^2}{2} \cdot \frac{f}{m} - \mathbf{R}_{r,2}^p$ // error of the predictor for coordinates
- $\mathbf{R}_r := \mathbf{R}_r^p + e_r \mathbf{C}_r$ // corrector for coordinates
- $t := t + h$

Test

The above formulas were implemented for a symmetric pair cation-anion. The equivalence of all formulations (ASPC written using history, ASPC Gear version 1, ASPC Gear version 2), as well as Verlet vs. 3-value Gear for coordinates, was verified. The figures show time development of the total energy, smoothed to suppress oscillations.



References

1. J. Kolafa: Time-Reversible Always Stable Predictor-Corrector Method for Molecular Dynamics of Polarizable Molecules, *J. Comput. Chem.* **25**, 335–342 (2004).
2. F. J. Vesely: N-particle dynamics of polarizable Stockmayer-type molecules, *J. Comput. Phys.* **24**, 361 (1977).
3. J. Genzer, J. Kolafa: Molecular dynamics of potential models with polarizability: comparison of methods, *J. Mol. Liq.* **109**, 63–72 (2004).
4. M. Sprik: A polarizable model for water using distributed charge sites, *J. Chem. Phys.* **95**, 6762–6769 (1991).
5. D. K. Remler, P. A. Madden, Molecular-dynamics without effective potentials via the Car-Parrinello approach, *Mol. Phys.* **70**, 921–966 (1990).
6. G. Lamoureux, B. Roux, Modeling induced polarization with classical Drude oscillators: Theory and molecular dynamics simulation algorithm, *J. Chem. Phys.* **119**, 3025–3039 (2003).

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