

Cell fluctuations in the TPCONTROL/DYNA VV2 modules

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1 Equations of motion

The constant-pressure, constant-temperature scheme of Equations (36) to (43) from Ref. [1] can be extended so that the scaling of the coordinates preserves the symmetry elements of a particular crystal system (or “Bravais lattice”).

1.1 Nonpolarizable force field

For a collection of N atoms with masses $\{m_i\}$, positions $\{\mathbf{r}_i\}$, velocities $\{\mathbf{v}_i\}$, and forces $\{\mathbf{F}_i\}$ ($i = 1, \dots, N$), the isothermal-isobaric equations of motion for *isotropic* volume fluctuations are the following:

$$\dot{\mathbf{r}}_i = \mathbf{v}_i + \dot{\boldsymbol{\varepsilon}} \mathbf{r}_i, \quad (1)$$

$$m_i \dot{\mathbf{v}}_i = \mathbf{F}_i - m_i (\dot{\eta} + a \dot{\boldsymbol{\varepsilon}}) \mathbf{v}_i, \quad (2)$$

$$Q \dot{\eta} = \sum_j m_j v_j^2 - N_f k_B T, \quad (3)$$

$$W \dot{\boldsymbol{\varepsilon}} = a \sum_j m_j v_j^2 + \sum_j \mathbf{F}_j \cdot \mathbf{r}_j - 3PV. \quad (4)$$

Variables $\dot{\eta}$ and $\dot{\boldsymbol{\varepsilon}}$ are associated to the constant-temperature and constant-pressure, respectively. Q and W are inertia parameters. N_f is the number of degrees of freedom, which corresponds to $3N$ minus the number of holonomic constraints, minus the number of translational invariances (3 if the atomic forces are conservative, 0 otherwise). Coefficient $a = 1 + 3/N_{\text{fp}}$, where N_{fp} is the number of degrees of freedom contributing to the pressure. For a nonpolarizable force field simulation, all degrees of freedom are contributing to the

pressure equally, and $N_{\text{fp}} = N_f$. Finally, T and P are the temperature and pressure of the reservoir, and k_B is Boltzmann’s constant.

These equations can be readily generalized by replacing the scalar variable $\dot{\boldsymbol{\varepsilon}}$ by a 3×3 tensor $\hat{\mathbf{E}}$ [2, 3].

$$\dot{\mathbf{r}}_i = \mathbf{v}_i + \hat{\mathbf{E}} \mathbf{r}_i, \quad (5)$$

$$m_i \dot{\mathbf{v}}_i = \mathbf{F}_i - m_i (\dot{\eta} + \hat{\mathbf{A}} \hat{\mathbf{E}}) \mathbf{v}_i, \quad (6)$$

$$Q \dot{\eta} = \sum_j m_j v_j^2 - N_f k_B T, \quad (7)$$

$$W \hat{\mathbf{E}} = \hat{\mathbf{A}} \sum_j m_j \mathbf{v}_j \mathbf{v}_j + \sum_j \mathbf{F}_j \mathbf{r}_j - lPV. \quad (8)$$

Scalar coefficient a has been replaced by the tensorial operator $\hat{\mathbf{A}} = l(1 + \text{tr}/N_{\text{fp}})$, with l the identity matrix and tr the trace operator. $\hat{\mathbf{A}}$ is applied to tensor $\hat{\mathbf{E}}$ in Eq. (6) and to dyadic tensor $\mathbf{v}_j \mathbf{v}_j$ in Eq. (8). We recover the equations of motion (1) to (4) if $\mathbf{E} = \varepsilon l$. In particular, Eq. (4) corresponds to the trace of Eq. (8).

Using the following definition of instantaneous pressure (corrected for the number of degrees of freedom contributing to it)

$$\tilde{P}V = \hat{\mathbf{A}} \sum_j m_j \mathbf{v}_j \mathbf{v}_j + \sum_j \mathbf{F}_j \mathbf{r}_j, \quad (9)$$

we can write Eq. (8) as

$$W \hat{\mathbf{E}} = (\tilde{\mathbf{P}} - lP)V. \quad (10)$$

Pressure tensor $\tilde{\mathbf{P}}$ is obtained from the instantaneous atomic velocities and forces, and is generally asymmetric. Used as such, it drives tensor $\hat{\mathbf{E}}$ to become asymmetric, which results in coordinates transformations that do not preserve the original shape of the simulation cell. To avoid transformations that would break the original symmetry of the simulation cell, we replace $\tilde{\mathbf{P}}$ with $\tilde{\mathbf{P}}_s$, which is a symmetrized form of the tensor calculated according to the crystal system:

$$\begin{array}{l} \text{Cubic :} \\ (a=b=c, \alpha=\beta=\gamma=90^\circ) \end{array} \quad \tilde{\mathbf{P}}_s = \begin{pmatrix} t_3 & 0 & 0 \\ 0 & t_3 & 0 \\ 0 & 0 & t_3 \end{pmatrix}, \quad (11)$$

$$\begin{aligned} \text{Tetragonal :} \\ (a=b, \alpha=\beta=\gamma=90^\circ) \end{aligned} \quad \tilde{\mathbf{P}}_s = \begin{pmatrix} t_{xy} & 0 & 0 \\ 0 & t_{xy} & 0 \\ 0 & 0 & \tilde{P}_{zz} \end{pmatrix}, \quad (12)$$

$$\begin{aligned} \text{Hexagonal :} \\ (a=b, \alpha=\beta=90^\circ, \gamma=120^\circ) \end{aligned} \quad \tilde{\mathbf{P}}_s = \begin{pmatrix} t_{xy} & 0 & 0 \\ 0 & t_{xy} & 0 \\ 0 & 0 & \tilde{P}_{zz} \end{pmatrix}, \quad (13)$$

$$\begin{aligned} \text{Rhombohedral :} \\ (a=b=c, \alpha=\beta=\gamma) \end{aligned} \quad \tilde{\mathbf{P}}_s = \begin{pmatrix} t_3 & s_3 & s_3 \\ s_3 & t_3 & s_3 \\ s_3 & s_3 & t_3 \end{pmatrix}, \quad (14)$$

$$\begin{aligned} \text{Orthorhombic :} \\ (\alpha=\beta=\gamma=90^\circ) \end{aligned} \quad \tilde{\mathbf{P}}_s = \begin{pmatrix} \tilde{P}_{xx} & 0 & 0 \\ 0 & \tilde{P}_{yy} & 0 \\ 0 & 0 & \tilde{P}_{zz} \end{pmatrix}, \quad (15)$$

$$\begin{aligned} \text{Monoclinic :} \\ (\alpha=\gamma=90^\circ) \end{aligned} \quad \tilde{\mathbf{P}}_s = \begin{pmatrix} \tilde{P}_{xx} & 0 & s_{zx} \\ 0 & \tilde{P}_{yy} & 0 \\ s_{zx} & 0 & \tilde{P}_{zz} \end{pmatrix}, \quad (16)$$

$$\text{Triclinic :} \quad \tilde{\mathbf{P}}_s = \frac{1}{2}(\tilde{\mathbf{P}} + \tilde{\mathbf{P}}^T), \quad (17)$$

with the following shorthand definitions: $t_3 = \frac{1}{3}(\tilde{P}_{xx} + \tilde{P}_{yy} + \tilde{P}_{zz})$, $t_{xy} = \frac{1}{2}(\tilde{P}_{xx} + \tilde{P}_{yy})$, $s_{zx} = \frac{1}{2}(\tilde{P}_{xz} + \tilde{P}_{zx})$, and $s_3 = \frac{1}{3}(s_{xy} + s_{yz} + s_{zx})$. Those symmetrized tensors preserve the crystal symmetry and have the same trace as the original pressure tensor.

For each crystal system, we indicate in parentheses the symmetry constraints imposed on the lattice parameters ($a, b, c, \alpha, \beta, \gamma$). The symmetrized tensor has a number of independent components equal to the number of lattice parameters allowed to fluctuate independently: only one for cubic systems, and at most 6 (for triclinic systems).

Constraints on bonds lengths are enforced with the SHAKE/Roll and RATTLE/Roll procedures of Martyna *et al.* [2], as explained in Ref. [1]. Those procedures iteratively calculate the Lagrange multipliers that keep the bond lengths constant and their time derivatives zero. The constraint forces contribute to the pressure through a virial term that we symmetrize according to Eqs. (11) to (17).

1.2 Drude polarizable force field

For a collection of N atoms individually coupled to N Drude particles with masses m_D , positions $\{\mathbf{r}_{D,i}\}$, velocities $\{\mathbf{v}_{D,i}\}$, and forces $\{\mathbf{F}_{D,i}\}$, the equations of motion can be cast in term of $\{\mathbf{R}_i\}$, the positions of the centers of mass of each pair, and of $\{\mathbf{d}_i\}$, the displacements of the Drude particles relative to their associated atom:

$$\dot{\mathbf{R}}_i = \mathbf{v}_{\mathbf{R},i} + \dot{\mathbf{E}}\mathbf{R}_i, \quad (18)$$

$$m_i \dot{\mathbf{v}}_{\mathbf{R},i} = \mathbf{F}_{\mathbf{R},i} - m_i (\dot{\eta} + \hat{\mathbf{A}}\dot{\mathbf{E}}) \mathbf{v}_{\mathbf{R},i}, \quad (19)$$

$$\dot{\mathbf{d}}_i = \mathbf{v}_{\mathbf{d},i} + \dot{\mathbf{E}}\mathbf{d}_i, \quad (20)$$

$$m_i \dot{\mathbf{v}}_{\mathbf{d},i} = \mathbf{F}_{\mathbf{d},i} - m'_i (\dot{\eta}_* + \hat{\mathbf{A}}\dot{\mathbf{E}}) \mathbf{v}_{\mathbf{d},i}, \quad (21)$$

$$Q\dot{\eta} = \sum_j m_j v_{\mathbf{R},j}^2 - N_f k_B T, \quad (22)$$

$$Q_* \dot{\eta}_* = \sum_j m'_j v_{\mathbf{d},j}^2 - N_{f_*} k_B T, \quad (23)$$

$$\begin{aligned} W\ddot{\mathbf{E}} &= \hat{\mathbf{A}} \sum_j (m_j \mathbf{v}_{\mathbf{R},j} \mathbf{v}_{\mathbf{R},j} + m'_j \mathbf{v}_{\mathbf{d},j} \mathbf{v}_{\mathbf{d},j}) \\ &+ \sum_j (\mathbf{F}_{\mathbf{R},j} \mathbf{R}_j + \mathbf{F}_{\mathbf{d},j} \mathbf{d}_j) - lPV. \end{aligned} \quad (24)$$

The “center-of-mass” variables \mathbf{R} and $\mathbf{v}_{\mathbf{R}}$, representing the atomic motions, are coupled to a thermostat “ η ” at room temperature T , while the “displacement” variables \mathbf{d} and $\mathbf{v}_{\mathbf{d}}$, representing dipole fluctuations, are coupled to a separate thermostat “ η_* ” at a temperature $T_* \ll T$. m_i is the mass of atom-Drude pair i , and m'_i is its reduced mass. Since the total pressure is primarily due to the N_f atomic degrees of freedom at room temperature, tensor $\hat{\mathbf{A}}$ is calculated using $N_{\text{fp}} = N_f$.

As for the nonpolarizable system, the tensor

$$\begin{aligned} \tilde{P}V &= \hat{\mathbf{A}} \sum_j (m_j \mathbf{v}_{\mathbf{R},j} \mathbf{v}_{\mathbf{R},j} + m'_j \mathbf{v}_{\mathbf{d},j} \mathbf{v}_{\mathbf{d},j}) \\ &+ \sum_j (\mathbf{F}_{\mathbf{R},j} \mathbf{R}_j + \mathbf{F}_{\mathbf{d},j} \mathbf{d}_j) \end{aligned} \quad (25)$$

is replaced by its appropriate symmetrized version.

2 Implementation in the TPCONTROL/DYNA VV2 modules

By default, volume fluctuations in the TPCONTROL/DYNA VV2 modules are isotropic, which means that the pressure is regulated by expanding or contracting the simulation cell uniformly in all directions. To access the “Parrinello-Rahman” generalization explained above, two additional keywords are available in the TPCONTROL module: FULL, which requests volume fluctuations consistent with the symmetry of the simulation cell, and ZONLy, which requests volume fluctuations along the z -axis only. ZONLy uses a truncated version of Eq. (24) in which only the zz component of $\ddot{\mathbf{E}}$ is nonzero.

References

- [1] Guillaume Lamoureux and Benoît Roux. Modeling induced polarization with classical Drude oscillators: Theory and molecular dynamics simulation algorithm. *J. Chem. Phys.*, 119(6):3025–3039, 2003.
- [2] Glenn J. Martyna, Mark E. Tuckerman, Douglas J. Tobias, and Michael L. Klein. Explicit reversible integrators for extended systems dynamics. 87(5):1117–1157, 1996.
- [3] M. Parrinello and A. Rahman. Crystal structure and pair potentials: A molecular-dynamics study. *Phys. Rev. Lett.*, 45(14):1196–1199, Oct 1980.