

Calculating the pressure in a molecular dynamics simulation in the presence of an applied electric field

The pressure of the system can be calculated from a single MD snapshot using Equation 3 of the main paper, reproduced here for convenience as Equation S1.

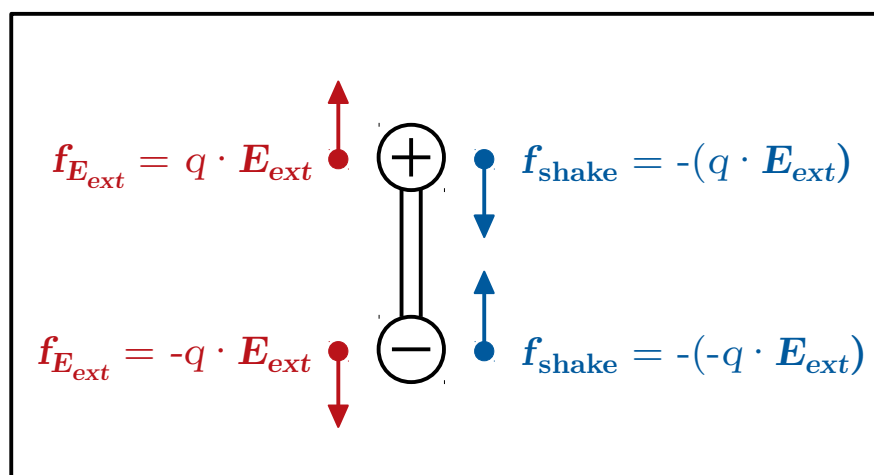
$$P = \frac{NkT}{V} + \frac{1}{3V} \sum_i \mathbf{r}_i \cdot \mathbf{f}_i \quad (\text{S1})$$

P is the pressure, N is the number of atoms, k is the Boltzmann constant, T is the temperature, V is the volume, \mathbf{r}_i is the position of atom i , and \mathbf{f}_i is the force acting on particle i .

In the presence of an external electric field, the forces acting on charged particles due to the applied field should be included in Equation S1. The reasons for this are illustrated in test cases 1 and 2 presented below. Test case 3 examines the requirements for the way the initial geometry must be specified in periodic MD simulations of a molecular liquid in the presence of an applied field.

Test case 1

A single, rigid, polar diatomic molecule, at rest, in a non-periodic cubic simulation cell



For a single molecule aligned with the field that does not interact with the boundaries of the simulation cell, the shake forces cancel the forces due to the electric field perfectly and keep the bond length fixed. The expected value of the total pressure in this scenario is zero, and the correct value is obtained if both the forces due to the external electric field and the forces that keep the bond length fixed are included in Equation S1. The same would hold for a “flexible” molecule at the equilibrium bond distance in the presence of the applied field.

If the forces due to the external electric field are not included Equation S1, then the calculated pressure will scale linearly with the strength of the applied field.

Test case 2

A gas of rigid, polar, diatomic molecules in a non-periodic cubic simulation cell

The table below summarizes the results of three simulations of a gas of 27 polar diatomic molecules in a $20 \times 20 \times 20$ nm cubic simulation cell. Randomized velocities were applied to all of the atoms at the start of each run, and then the simulations were performed at constant volume and constant energy. In each case, three different methods were used to calculate the pressure inside the simulation cell: the ideal gas law, direct measurement of the forces on the boundary walls ($P = F/A$), and Equation S1.

	$E = 0.0 \text{ V/\AA}$	$E = 1.0 \text{ V/\AA}$	
		Forces due to E-field included in Eqn. 1	Forces due to E-field not included in Eqn. 1
Average temperature	612 K	614 K	627 K
Pressure (ideal gas law)	$2.85 \times 10^4 \text{ Pa}$	$2.86 \times 10^4 \text{ Pa}$	$2.92 \times 10^4 \text{ Pa}$
Pressure (forces on boundary walls)	$2.91 \times 10^4 \text{ Pa}$	$2.87 \times 10^4 \text{ Pa}$	$2.96 \times 10^4 \text{ Pa}$
Pressure (Equation 1)	$2.88 \times 10^4 \text{ Pa}$	$2.77 \times 10^4 \text{ Pa}$	$-1.42 \times 10^5 \text{ Pa}$

If the terms due to the external field are excluded from Equation 1, a large negative pressure is erroneously obtained. In simulations of a polar liquid at constant pressure this would cause the density of the liquid to increase, until the fictitious negative contribution to the pressure is cancelled out by the repulsive forces between the molecules of the compressed liquid.

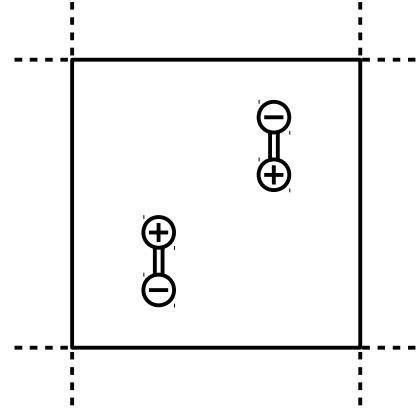
Test case 3

Two rigid, polar, diatomic molecules, at rest, in a periodic simulation cell

The examples given below illustrate why care needs to be taken, when defining the geometry in runs with an applied electric field and a periodic simulation cell. Three different ways of specifying the same periodic structure (except for a shift in the origin) are illustrated below. The positions of the atoms are specified in the format used in the LAMMPS data file. The simulation cell is a cube with corners at (0,0,0), (10,0,0), (0,10,0), (0,0,10), etc.

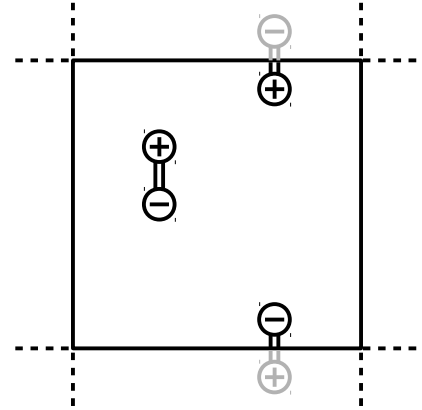
Input 1:

ID	molecule	type	charge	x	y	z
1	1	1	-1	3.0	0.0	2.0
2	1	2	1	3.0	0.0	4.0
3	2	1	-1	7.0	0.0	8.0
4	2	2	1	7.0	0.0	6.0



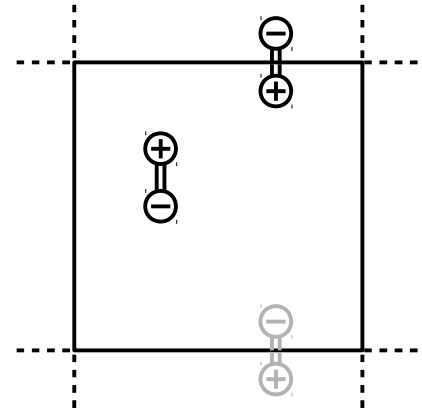
Input 2:

ID	molecule	type	charge	x	y	z
1	1	1	-1	3.0	0.0	5.0
2	1	2	1	3.0	0.0	7.0
3	2	1	-1	7.0	0.0	1.0
4	2	2	1	7.0	0.0	9.0



Input 3:

ID	molecule	type	charge	x	y	z	nx	ny	nz
1	1	1	-1	3.0	0.0	5.0	0	0	0
2	1	2	1	3.0	0.0	7.0	0	0	0
3	2	1	-1	7.0	0.0	1.0	0	0	1
4	2	2	1	7.0	0.0	9.0	0	0	0



The energy of interaction between the system and the applied field is calculated as

$$P.E. = -\sum_i \mathbf{r}_i \cdot q_i \mathbf{E}_{ext} \quad (S2)$$

Alternatively, it can be calculated from the molecular dipoles, $\boldsymbol{\mu}$:

$$P.E. = -\sum_j \boldsymbol{\mu}_j \cdot \mathbf{E}_{ext} \quad (S3)$$

In the structures specified in inputs 1-3, P.E. = 0, because $\mu_1 = -\mu_2$. When Equation S2 is used to calculate the energy, the correct value of zero is obtained for input 1, but not for input 2. This discrepancy is just another example of the well-known problems that can arise when applying classical concepts of polarization to periodic systems. For a detailed discussion of this matter, the reader is directed to e.g. N.A. Spaldin, *Journal of Solid State Chemistry* 195, pp. 2 (2012). However, in the present case, consistency between equations S2 and S3 can be ensured by simply requiring that the geometry should be specified such, that all molecules remain “intact”. Whenever a molecule crosses a boundary of the simulation cell, it is therefore necessary to specify, which atoms lie “outside” of the first simulation cell.

In input 3, the nx , ny , and nz values specify that atom 3 is not in the first simulation cell, but in the next one along the positive direction of the z -axis. The absolute position of atom 3 is thus (7.0, 0.0, 11.0). When the absolute positions of all of the atoms are used to calculate the energy of interaction between the system and the external field, the correct value of zero is obtained.

In LAMMPS, all events where an atom crosses a boundary of the simulation cell are tracked, so it is easy to ensure that meaningful results will be obtained by simply defining the initial structure such, that all molecules are entirely within one simulation cell. If a snapshot from a previous run is used as the initial geometry, then the nx , ny , and nz values of each atom must be provided.

The discussion presented above also applies to the contribution of the electric field terms to pressure virial, as the virial term is equal to $-1/3V$ times the right hand side of Equation S2.