Comments on the Manuals of the GROMACS and LAMMPS software packages

Gang Liu
gang.liu@queensu.ca, gl.cell@outlook.com
Centre for Advanced Computing (HPCVL)
Queen's University, Kingston, Ontario, Canada

(Dated: November 15, 2016)

The GROMACS and LAMMPS [1, 2]

are freely-available and very widely-used software packages for molecular dynamics (MD) simulations in various research fields. Their manuals are very helpful for users. Here I would like to address a few issues in the "GROMACS Reference Manual Version 2016" and "LAMMPS Users Manual 30 Jul 2016 version" and refer to them as the GROMACS Manual and the LAMMPS Manual, respectively.

ITEM 1. Equation (4.2) on page 65 of the GROMACS Manual:

$$\mathbf{F}_i = -\sum_j \frac{dV_{ij}(r_{ij})}{dr_{ij}} \frac{\mathbf{r}_{ij}}{r_{ij}} = -\mathbf{F}_j,$$

is not true. Since j is the summation index, it should not appear on the right side.

ITEM 2. The virial part of the internal pressure/stress can not be expressed as Equation (A.11) on page 216 of the GROMACS Manual. As shown in Equation (A.12), the force $\mathbf{F}_i$ is the net one acting on particle i from all other particles. Equation (A.11) is a linear combination of the $\mathbf{F}_i$ forces. When the system is in an equilibrium state, all $\mathbf{F}_i$ forces are zero (no external forces act on the internal MD particles directly under periodic boundary conditions), so is Equation (A.11). This is not correct for the actual virial part. The problem occurs in the step from Equation (A.8) to Equation (A.9). Equation (A.3) on page 215 shows the "distance vector of the nearest image of atom i from atom j",

$$\mathbf{r}_{ij}^n = \mathbf{r}_i + \delta_i - \mathbf{r}_j,$$

where δ_i is the "shift vector to the position vector $\mathbf{r}_i$ of atom i". As a matter of fact, even for the same atom i, but for different atom j, the shift vector δ_i may be different. In other words, the shift vector depends on both i and j. It should therefore be written as δ_{ij}, rather than δ_i. Since $\delta_{ij} = -\delta_{ji}$ and $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$, Equation (A.5) may be written as

$$\begin{aligned}
\Xi &= -\frac{1}{2}\sum_{i<j}^{N} \mathbf{r}_{ij}^n \otimes \mathbf{F}_{ij} \\
&= -\frac{1}{2}\sum_{i<j}^{N} (\mathbf{r}_i + \delta_{ij} - \mathbf{r}_j) \otimes \mathbf{F}_{ij} \\
&= -\frac{1}{2}\sum_{i<j}^{N} \mathbf{r}_i \otimes \mathbf{F}_{ij} + \frac{1}{2}\sum_{i<j}^{N} \mathbf{r}_j \otimes \mathbf{F}_{ij} + \\
&\quad -\frac{1}{2}\sum_{i<j}^{N} \delta_{ij} \otimes \mathbf{F}_{ij} \\
&= -\frac{1}{2}\sum_{i<j}^{N} \mathbf{r}_i \otimes \mathbf{F}_{ij} - \frac{1}{2}\sum_{k<l}^{N} \mathbf{r}_l \otimes \mathbf{F}_{lk} + \\
&\quad -\frac{1}{4}\sum_{i<j}^{N} \delta_{ij} \otimes \mathbf{F}_{ij} - \frac{1}{4}\sum_{k<l}^{N} \delta_{lk} \otimes \mathbf{F}_{lk} \\
&= -\frac{1}{2}\sum_{i<j}^{N} \mathbf{r}_i \otimes \mathbf{F}_{ij} - \frac{1}{2}\sum_{l>k}^{N} \mathbf{r}_l \otimes \mathbf{F}_{lk} + \\
&\quad -\frac{1}{4}\sum_{i<j}^{N} \delta_{ij} \otimes \mathbf{F}_{ij} - \frac{1}{4}\sum_{l>k}^{N} \delta_{lk} \otimes \mathbf{F}_{lk} \\
&= -\frac{1}{2}\sum_{i}^{N}\sum_{j}^{N} \mathbf{r}_i \otimes \mathbf{F}_{ij} - \frac{1}{4}\sum_{i}^{N}\sum_{j}^{N} \delta_{ij} \otimes \mathbf{F}_{ij} \\
&= \Xi_0 + \Xi_1,
\end{aligned}$$

where

$$\begin{aligned}
\Xi_0 &= -\frac{1}{2}\sum_{i}^{N} \mathbf{r}_i \otimes \sum_{j}^{N} \mathbf{F}_{ij} = -\frac{1}{2}\sum_{i}^{N} \mathbf{r}_i \otimes \mathbf{F}_i, \\
\Xi_1 &= -\frac{1}{4}\sum_{i}^{N}\sum_{j}^{N} \delta_{ij} \otimes \mathbf{F}_{ij}.
\end{aligned}$$

When the system is in an equilibrium state, all $\mathbf{F}_i$ forces are zero, then $\Xi_0 = 0$. However, Ξ_1 can take any value depending on the external environment. Essentially, Ξ_1 is the main interaction tensor, Equations (7-11), in [3]. Thompson *et al* also showed the same as in Equation (31) in [5]. In any case, Ξ_1 cannot be written as

$$-\frac{1}{4}\sum_{i}^{N} \delta_{ij} \otimes \mathbf{F}_i.$$

Additionally the $i = j$ case is not considered in the GROMACS Manual due to the "minimum image convention". In [3] and [5], for general situations, the "minimum image convention" is not used, but all forces are considered.

The same problem occurs in the "compute pressure command" section on page 1207 of the LAMMPS Manual.

ITEM 3. Gromacs supports the usage of the "Parrinello-Rahman pressure coupling" by using Equation (3.61) on page 36 of the GROMACS Manual, which is the dynamical equation of the **b** "box vectors":

$$\ddot{\mathbf{b}} = VW^{-1}\mathbf{b}'^{-1}\left(\mathbf{P} - \mathbf{P}_{ref}\right).$$

Let us call this equation the KEY equation. Assuming that $\mathbf{b}'$ is the transpose of $\mathbf{b}$, $V\mathbf{b}'^{-1}$ is a surface area vector of a cell. Normally the kinetic energy term of the internal pressure/stress is based on the true kinetic energy as in Equations (3.21) and (3.22) on page 25 of the Gromacs manual. But the corresponding one in Parrinello-Rahman theory is based on the kinetic energy relative to the box vectors (see the line after Equation (4) in their paper [6]). Further ignoring this difference, the KEY equation is equivalent to Equation (3) for the case of constant external pressure of Parrinello-Rahman theory [6]. However the KEY equation is still quite different from the corresponding one in Parrinello-Rahman theory for the case of constant external stress, Equation (2.25) of their original paper [7].

On page 751 of the LAMMPS Manual, during solving the Parrinello-Rahman's dynamical equation of the period vectors under external stress, LAMMPS has the idea to reset the "reference dimensions" with the current one. If this is done throughout, Equation (2.25) of Parrinello-Rahman theory for the case of constant external stress [7] reduces to the KEY equation.

However, as stated on page 36 of the GROMACS Manual, in order to use the KEY equation, the equations of motion for the particles should also be changed to

$$m_i\ddot{\mathbf{r}}_i = \mathbf{F}_i + \overrightarrow{f_i},$$

with $\overrightarrow{f_i} = -m_i\mathbf{b}^{-1}\left(\dot{\mathbf{b}}\mathbf{b}' + \mathbf{b}\dot{\mathbf{b}'}\right)\mathbf{b}'^{-1}\dot{\mathbf{r}}_i$, based on Parrinello-Rahman theory [6, 7]. One may notice that the friction-style force $\overrightarrow{f_i}$ acting on the particles in the above equation is ficticious. As a matter of fact, there is no such friction. The question is whether it should be there.

Now let us clarify a few terms. For a variety of reasons, periodic boundary conditions are often applied to a finite system. Then the original system becomes a cell at the center, called the MD cell. All particles in the MD cell are called MD particles. Dynamical equations are needed for the MD particles and the period (box) vectors. The external pressure/stress is supposed to only act on the infinitely far-away surfaces of the whole system of unlimited number of such cells, not on the MD particles directly. A reasonable solution would be: 1) the MD particles obey Newton's Second Law with real forces only (no ficticious forces) and 2) the influence of external pressure/stress is implemented, explicitely only in the dynamical equation of the box/period vectors. Once the box/period vectors are affected by the external pressure/stress directly, they would also influence the forces on the MD particles, since the distances of particles depend on the box/period vectors. This way, the external pressure/stress influence the motion of the whole system (see [3, 4]).

The purpose of [3] was to derive the dynamical equation of the box/period vectors (Equation (27) in the paper):

$$\alpha_{\mathbf{h},\mathbf{h}}\ddot{\mathbf{h}} = \left(\overrightarrow{\overrightarrow{\pi}} + \overrightarrow{\overrightarrow{\Upsilon}}\right)\cdot\sigma_{\mathbf{h}}, \quad (\mathbf{h} = \mathbf{a}, \mathbf{b}, \mathbf{c}),$$

which is essentially the same as the above KEY equation. In the derivation, no kinetic energy relative to the box vectors is needed, no reference dimensions are introduced, and no ficticious forces appear. All equations are for the general external stress case, also applicable for external pressure as a special one. The Newton's Second Law is applied on the MD particles,

$$m_i\ddot{\mathbf{r}}_i = \mathbf{F}_i.$$

The KEY equation is important in the manuals, but was not formally published before. Those who want to use the KEY equation and prefer the freedom to use Newton's Second Law on the MD particles, should consult [3, 4]. Since only pure mechanics are considered there, the Berendsen or Velocity-rescaling temperature coupling can be applied additionaly.

[1] http://www.gromacs.org
[2] http://lammps.sandia.gov
[3] G. Liu, Can. J. Phys. **93**, 974 (2015), dx.doi.org/10.1139/cjp-2014-0518
[4] G. Liu, arXiv:cond-mat/0209372v16.
[5] A. P. Thompson, S. J. Plimpton, and W. Mattson, J. Chem. Phys. **131**, 154107 (2009), doi: 10.1063/1.3245303
[6] M. Parrinello, and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980), doi:10.1103/PhysRevLett.45.1196.
[7] M. Parrinello, and A. Rahman, J. Appl. Phys. **52**, 7182 (1981), doi:10.1063/1.328693.