Calculation of pressure in case of periodic boundary conditions

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Abstract

It has long been standard practice to calculate the pressure in molecular simulations using the virial equation. However, in this Letter, we show that the virial equation does not apply when periodic boundary conditions are used. For pair-additive forcefields the problem is easily circumvented, but when non pair-additive forcefields are used, the virial equation should not be used for periodic systems. Examples of calculations for which errors could arise are simulations with polarizable forcefields or with ab initio molecular dynamics. Readers are warned not to use the virial equation in cases where it does not apply.
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1. Introduction

In molecular dynamics (MD) or Monte Carlo (MC) simulations, it is common practice to calculate the pressure in the system, either in order to perform constant pressure (NPT) simulations, or simply to monitor it. The method of calculating the pressure is basically to sum over the forces on all atoms according to the virial equation:

$$P = \frac{Nk_{B}T}{V} + \frac{1}{3V}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i \right\rangle \quad (1)$$

where k_{B} is Boltzmann's constant, $\mathbf{f}_i$ is the force on atom i due to all other atoms, and $\langle \ldots \rangle$ denotes the statistical average over time. However, this method breaks down when periodic boundary conditions are applied. With this Letter, we hope to warn readers not to use the virial equation in cases where it does not apply.

For pair-additive forcefields the virial equation is usually written as

$$P = \frac{Nk_{B}T}{V} + \frac{1}{6V}\left\langle \sum_{i=1}^{N} \sum_{j\neq i}^{N} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle \quad (2)$$

where $\mathbf{f}_{ij}$ is the force on atom i due to atom j and $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$.

Fortuitously, Eq. (2) continues to hold when using periodic boundary conditions, so for many classical simulations there is no problem, because most simulations are still performed with pair-additive forcefields. However, whenever non pair-additive forcefields or ab initio energies are used in combination with periodic boundaries, the virial equation should not be applied to calculate the pressure in the system.

In this Letter, we will first give a derivation of Eq. (1) and explain why Eq. (1) is incorrect for systems with periodic boundaries. Next, we will show how Eq. (2) for pair-additive forcefields is usually derived from Eq. (1), and why this derivation is flawed under periodic boundary conditions. We will then give a correct derivation for the pressure for pair-additive forcefields, and show that Eq. (2) still holds. A compensation of errors in the flawed scheme leads – by coincidence – to the correct outcome. This has led to unjustified confidence in Eq. (1), and applications of the virial equation in cases where it does not hold. Although examples of correct pressure calculations are also available in the literature [1,2], we feel an explicit warning is warranted. A first warning that the virial equation is not complete for periodic systems was published in 1983 [3].

Finally, because readers might find it hard to believe that the virial equation does not apply in all cases, we give a simple example for which it fails.

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2. Derivation of the virial equation

From thermodynamics it is known that the pressure is equal to the derivative of the total energy, E, with respect to the volume, V, at constant temperature, T (see any physical chemistry textbook):

$$P = -\left(\frac{dE}{dV}\right)_T \tag{3}$$

The total energy can be divided into the kinetic energy, K, and the potential energy, U. Applying this decomposition to Eq. (3), and taking a statistical average gives

$$P = \frac{Nk_BT}{V} - \left\langle\frac{dU}{dV}\right\rangle \tag{4}$$

The first term on the right-hand side is the kinetic derivative term, which is given by the ideal gas law. To evaluate the potential derivative term, we use that for periodic systems the potential energy per unit cell is a function of the atomic positions $(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) \equiv \mathbf{r}^N$ of the N atoms in the unit cell, and the box length L:

$$U = U(\mathbf{r}^N, L) \tag{5}$$

With the positions of the atoms in a single unit cell given, the box length can be used to establish the positions of atoms in all periodic images of the unit cell, and hence the potential energy. For simplicity, we assume a cubic periodic box with length L that is scaled uniformly; obviously a similar derivation could be performed for differing lattice vectors, and a generalization to the various terms of the stress tensor is also straightforward.

The derivative of U with respect to V has contributions due to the variation of U with respect to L with the atom positions fixed (bringing the atoms in one cell closer to the atoms in another cell), and the variation of U due to the scaling of atom positions with L: $\mathbf{r}_i = \mathbf{s}_i L$. Using the chain rule we obtain

$$\begin{aligned}
\frac{dU}{dV} &= \frac{dL}{dV}\left(\frac{\partial U}{\partial L} + \sum_{i=1}^{N}\frac{d\mathbf{r}_i}{dL} \cdot \frac{\partial U}{\partial \mathbf{r}_i}\right) \\
&= \frac{1}{3L^2}\left(\frac{\partial U}{\partial L} + \sum_{i=1}^{N}\frac{\mathbf{r}_i}{L} \cdot \frac{\partial U}{\partial \mathbf{r}_i}\right) \\
&= \frac{1}{3V}\sum_{i=1}^{N}\mathbf{r}_i \cdot \frac{\partial U}{\partial \mathbf{r}_i} + \frac{1}{3L^2}\frac{\partial U}{\partial L}
\end{aligned} \tag{6}$$

Now using the definition of the force on atom i, $\mathbf{f}_i$:

$$\mathbf{f}_i = -\frac{\partial U}{\partial \mathbf{r}_i} \tag{7}$$

and substituting Eqs. (6) and (7) into Eq. (4), we obtain the correct form of the virial equation:

$$P = \frac{Nk_BT}{V} + \left\langle\frac{1}{3V}\sum_{i=1}^{N}\mathbf{r}_i \cdot \mathbf{f}_i - \frac{1}{3L^2}\frac{\partial U}{\partial L}\right\rangle \tag{8}$$

In these equations, the full derivatives of U (dU/dV and dU/dL) denote the dependence of U on the box length L

with scaling of the atomic coordinates included, and the partial derivative $\partial U/\partial L$ is the dependence on L without scaling of atomic coordinates.

For non-periodic systems, for which the potential energy does not depend on the size of an enclosing box, the term containing $\partial U/\partial L$ is zero. Changing the box length without also changing the atomic coordinates has no effect in a non-periodic system, and we arrive back at the standard virial equation (Eq. (1)).

However, when periodic boundary conditions are used, the additional term is not zero. Increasing the box length without varying the atomic coordinates would still lead to an increase in the distance between the particles in different copies of the box, and the partial derivative $\partial U/\partial L$ will have a finite value. As a result, we conclude that under periodic boundary conditions Eq. (1) does not hold.

3. The special case of pair-additive forcefields

In the special case of pair-additive forcefields, the virial equation is usually written in a pair wise manner (Eq. (2)). This is probably the most commonly used form of the virial equation. Although Eq. (1) is incorrect under periodic boundary conditions, Eq. (2) is correct even for periodic boundary conditions.

In this section, we will first give the common derivation of Eq. (2) from Eq. (1) for non-periodic systems, and explain why this derivation does not hold for periodic systems. Then, we will give the correct derivation and show that Eq. (2) does apply. Apparently, errors in the flawed derivation cancel out to give the correct result.

The standard derivation begins by writing the force on atom i due to all other atoms:

$$\mathbf{f}_i = \sum_{j \neq i}^{N}\mathbf{f}_{ij} \tag{9}$$

When we substitute this into Eq. (1), we get

$$P = \frac{Nk_BT}{V} + \frac{1}{3V}\left\langle\sum_{i=1}^{N}\sum_{j \neq i}^{N}\mathbf{r}_i \cdot \mathbf{f}_{ij}\right\rangle \tag{10}$$

In this equation, we can permute the indices i and j resulting in

$$P = \frac{Nk_BT}{V} + \frac{1}{3V}\left\langle\sum_{j=1}^{N}\sum_{i \neq j}^{N}\mathbf{r}_j \cdot \mathbf{f}_{ji}\right\rangle \tag{11}$$

Now using $\mathbf{f}_{ij} = -\mathbf{f}_{ji}$, and adding the two equivalent right-hand sides of Eqs. (10) and (11), and dividing by 2, we arrive at the following equation:

$$P = \frac{Nk_BT}{V} + \frac{1}{6V}\left\langle\sum_{i=1}^{N}\sum_{j \neq i}^{N}\mathbf{r}_{ij} \cdot \mathbf{f}_{ij}\right\rangle \tag{2}$$

However, for periodic systems this derivation is not correct, because the assumption going from Eq. (10) to Eq. (11) no longer applies. With periodic boundary conditions, the total force on atom i is not only due to all other atoms

in the original unit cell, but to *all* other atoms, including those in the periodic copies of the unit cell. If we now introduce the number of periodic copies M (which is, in principle, infinite) into Eq. (9), we get

$$\mathbf{f}_i = \sum_{j \neq i}^{MN} \mathbf{f}_{ij} \tag{12}$$

The equivalent of Eq. (10) then becomes

$$P = \frac{N k_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{MN} \mathbf{r}_i \cdot \mathbf{f}_{ij} \right\rangle \tag{13}$$

And we see that the indices i and j are no longer equivalent and thus cannot be permuted.

To perform a correct derivation of the pressure in periodic systems for pair-additive forcefields, we begin with the potential energy per unit cell:

$$U = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{MN} U_{ij}(\mathbf{r}_{ij}) \tag{14}$$

where U_{ij} is the contribution to the energy U of the interaction between the atoms i and j. Note that in this relation there is no explicit dependence on L; the only dependence on L is implicit via scaling of $\mathbf{r}_{ij}$. When atoms i and j are in the same unit cell, it is evident that the derivative of interatomic distance with L is $\mathrm{d}\mathbf{r}_{ij}/\mathrm{d}L = \mathbf{r}_{ij}/L$, but this is true even when they are in different cells. For instance, if atom j is in the cell with its origin at position $\mathbf{R}_n = (n_x \mathbf{e}_x + n_y \mathbf{e}_y + n_z \mathbf{e}_z)L \equiv \mathbf{n}L$, then $\mathbf{r}_{ij} = (\mathbf{s}_i - \mathbf{s}_j - \mathbf{n})L$, and again $\mathrm{d}\mathbf{r}_{ij}/\mathrm{d}L = \mathbf{r}_{ij}/L$. Therefore, the derivative of U is

$$\frac{\mathrm{d}U}{\mathrm{d}V} = \frac{1}{2} \frac{\mathrm{d}L}{\mathrm{d}V} \sum_{i=1}^{N} \sum_{j \neq i}^{MN} \frac{\mathrm{d}\mathbf{r}_{ij}}{\mathrm{d}L} \cdot \frac{\partial U}{\partial \mathbf{r}_{ij}} = \frac{1}{6L^2} \sum_{i=1}^{N} \sum_{j \neq i}^{MN} \frac{\mathbf{r}_{ij}}{L} \cdot \frac{\mathrm{d}U_{ij}}{\mathrm{d}\mathbf{r}_{ij}}$$

$$= \frac{-1}{6V} \sum_{i=1}^{N} \sum_{j \neq i}^{MN} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \tag{15}$$

Now we can substitute Eq. (15) into Eq. (4), and we arrive at Eq. (2), suitably modified for the energy per unit cell in a periodic system. So Eq. (2) proves to be correct after all, even when periodic boundary conditions are applied. Apparently, the error introduced in the derivation of Eq. (2) from the erroneous Eq. (1) leads to the correct result. Because of the erroneous derivation, however, this correct result does not prove the starting point, Eq. (1), to be right.

It is very fortunate that Eq. (2) is correct for periodic systems, because this form of the virial equation has been used in a vast number of simulations. However, since Eq. (1) is not correct for periodic systems, any simulation code that uses that form of the virial equation to calculate the pressure in a periodic system will give an incorrect pressure.

4. A simple example

In the previous sections, we have shown that the virial equation (Eq. (1)) is not correct for systems with periodic boundary conditions, but for the special case of pair-addi-
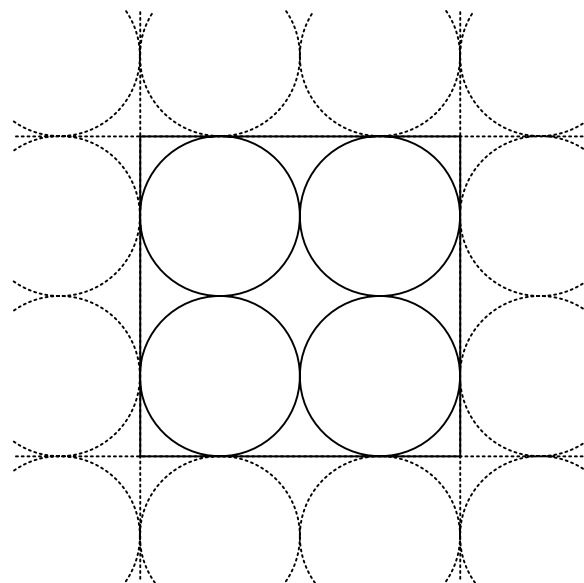

Fig. 1. Example of a system for which the error in the virial equation is obvious: an infinite perfect lattice.

tive forcefields (Eq. (2)), the equation can be applied to periodic systems. Thus, whenever the energy calculation is not pair-additive the virial equation should not be used for periodic systems. To demonstrate this, we will now give a simple example that shows that indeed Eq. (1) cannot be applied under periodic boundary conditions.

Consider a small periodic box with four atoms on a perfect lattice (Fig. 1), with a purely repulsive pair wise interaction between the atoms. Take the system to be at zero temperature (i.e., there is no thermal motion), and suppose that it is strongly compressed. The pressure in this system is highly positive because of the repulsion between the atoms. Now, when we calculate the force on an atom, it will be zero because of the infinite perfect lattice. Substituting these zeros in Eq. (1) we would find only the ideal gas term, i.e., $P = 0$ at $T = 0$, which is obviously not correct.

When Eq. (2) is used to calculate the pressure in this example, we do obtain a high positive value for the pressure. We conclude that Eqs. (1) and (2) are indeed different, and that Eq. (1) is giving incorrect results for periodic systems. Adding the $\partial U / \partial L$ term (Eq. (8)) will lead to the correct result.

5. Discussion

We have shown that the virial equation in its original form (Eq. (1)) is not applicable when periodic boundary conditions are used. Our intent is firstly to warn readers of this, and secondly, to point out that there is no simple method to calculate the pressure in periodic systems. The only way to calculate the pressure in a periodic system is either to directly evaluate Eq. (4) numerically, or to take the analytical derivative of the potential energy, using Eq. (8). Either way requires much effort.

Fortunately, for most classical simulations pair-additive forcefields are used, and for these simulations there is no problem. Nevertheless, there is a potential pitfall: because in molecular dynamics the net forces on the atoms are calculated in order to facilitate Newtonian dynamics, one might be tempted to use these atomic forces to calculate the pressure via Eq. (1).

An example of a situation where real problems could be expected is when polarizable forcefields are used. In that case, the energy is not pair wise additive and the only way to calculate the pressure is to use Eq. (4) or (8). Note that even when the implementation is such that, after evaluating the polarization, the energy is calculated in a pair wise manner (i.e., calculating the Coulombic interactions with the induced dipoles), Eq. (2) cannot be used. This is because the induced dipoles depend on all atomic positions, and U_{ij} is not a function of only $\mathbf{r}_{ij}$ but depends on all $\mathbf{r}^N$, so Eq. (15) is not applicable.

Another area for which our conclusions apply is ab initio calculations with periodic boundary conditions. To calculate the pressure it is necessary to evaluate the full derivative of the energy with respect to the volume. This demands a huge effort, but there are a few examples where it has been done [4–7]. Readers who might be tempted to calculate the pressure in a classical way, using just the forces $\mathbf{f}^N$ on the nuclei, should be warned again that the virial equation as it is written in Eq. (1) is not correct for periodic systems. One should use Eq. (8), which contains the $\partial U/\partial L$ term.

An alternative that is as simple as the virial equation, but which also holds for periodic boundary conditions, would be very welcome.

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