Prediction for Fluid’s Transport Coefficients due to Pressure Results with MDS under Periodic Boundary Conditions

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Abstract. Periodic boundary conditions are usually used to calculate the transport coefficients for equilibrium state molecular dynamics simulation, among which pressure is a basic and crucial parameter. Aiming at the rationality and stability of the pressure calculation results for periodic boundary conditions, the Virial formula is thought over from derivation process, and simulation factors affecting the pressure results are analyzed with a mass of data. Basing on the pressure control method, the zero shear viscosity simulation conditions are deduced and the reasonable results are obtained to verify the feasibility of pressure calculation in turn, it will be a useful reference for transport coefficients simulation as the pressure and zero shear viscosity simulation under periodic boundary.

1. Introduction
For molecular dynamics simulation of fluid, the pressure is the basic parameter equivalent to the stress calculation for solid model, and the simulation of the shear viscosity and other transport parameters is based on the results of the shear pressure. The stability and accuracy of the pressure calculation directly affect the results of other transport parameters. It is of great significance to discuss the impact factors of pressure calculation and find the final simulation conditions of pressure calculation.

Molecular dynamics studies on transport coefficients can be divided into two ways: equilibrium state molecular dynamics and non-equilibrium state molecular dynamics. With the equilibrium state molecular dynamics simulation, the transport coefficient is calculated by Green-Kubo formula or the corresponding Einstein formula which depends on the principle of statistical mechanics and time-dependent function. On the other hands for the non-equilibrium molecular dynamics method, appropriate perturbation is applied to the system, and the transport coefficient is calculated based on the effect of the perturbation on the system.

At present, Virial equation \([1]\) is often used to calculate the pressure of a fluid in equilibrium state molecular dynamics method, as follows:

\[
P = \frac{1}{3V} \sum_{\alpha=1}^{3} < \sum_{i=1}^{n} m_i V_{1\alpha} V_{1\alpha} + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij\alpha} F_{ij\alpha} >
\]

Where \(m_i\) is the mass of the molecule \(i\), \(r_{ij\alpha}\) and \(f_{ij\alpha}\) are the displacement vector and the force vector respectively between molecular \(i\) and \(j\) in the direction of the component \(\alpha\); \(n\) and \(V\) are the molecule number and volume of the system; \(< >\) means the ensemble average. Due to the Quasi Ergodicity hypothesis in the molecular dynamics simulation, the ensemble average is equivalent to the time average.

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In the formula (1), the first term \( \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} m_i v_{i,j} v_{i,j} > \) indicates the effect of particle kinetic energy on the pressure, the second term \( \frac{1}{3} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} f_{i,j,k} > \) indicates the effect of the force between the particles on pressure. For the kinetic energy term of the solid medium, it is much smaller than the force term, but for the liquid and gaseous medium Kinetic energy has played a leading role \(^2\). Fluid model has strong fluidity, and its pressure calculation is different from the solid model, even with the same calculation model, when the calculation conditions change, the pressure results also have a greater change \(^3\).

By discussing the Virial equation, different opinions have been put forward. Irving and Kirkwood \(^4\) and Hardy \(^5\) proposed a new Virial equation with the correcting kinetic energy terms in consideration of the relationship between the particle velocity and the model velocity. Recently, Zhou \(^6\) \( ^7\) disagreed on the first kinetic term in the Virial equation, by discussing the stress formula between Cauchy stress and molecular dynamics for continuous media, he argued that stress calculation should not be related to the kinetic energy of particles, the kinetic energy term should be removed from pressure calculation.

Many conditions have been put forward by many scholars on the applicability of the Virial equation. Especially for the application on periodic boundary conditions, there is still some controversy \(^8\). In this paper, the liquid argon model is simulated under the equilibrium periodic conditions, with analysing the influence factors on the pressure results, the applicability of the Virial equation is discussed under the periodic boundary conditions, and the viscosity result is used to verify the rationality of pressure calculation.

2. **Pressure formula’s derivation for molecular dynamics simulation**

In order to understand the meaning of each term in Virial equation, the derivation process will be discussed. There are several versions, in this paper, the two typical derivations are listed. The first one is derived from the Virial functions primordially the Virial function is put forward as the shape function of the simulation system \(^9\):

\[
I = \frac{1}{2} \sum_{i=1}^{n} m_i \cdot v_i \tag{2}
\]

If the shape of the system does not change during the simulation, the second derivative is zero:

\[
\frac{d^2 I}{dt^2} = \sum_{i=1}^{n} m_i \cdot \ddot{v}_i + \sum_{i=1}^{n} m_i \cdot v_i \cdot \ddot{v}_i = 0 \tag{3}
\]

According to Newton's second law and the mean of time, then:

\[
< \sum_{i=1}^{n} m_i \cdot \dot{v}_i > +< \sum_{i=1}^{n} m_i \cdot \ddot{v}_i >= 0 \tag{4}
\]

The forces acting on the system include the interaction between particles and the effect from the external system. That is, the pressure of the system:

\[
< \sum_{i=1}^{n} m_i \cdot \dot{v}_i > =< \sum_{i=1}^{n} F_i \cdot \dot{v}_i >
\]

\[
= \frac{m}{3} \left( \sum_{i=1}^{n} \sum_{j=1}^{n} (F_{i,j} \cdot \dot{v}_{i,j} + F_{j,i} \cdot \dot{v}_{j,i} + F_{k,i} \cdot \dot{v}_{k,i}) > >
\]

\[
= \frac{m}{3} \left( \sum_{i=1}^{n} \sum_{j=1}^{n} (\overline{F_{i,j}} \cdot \dot{v}_{i,j}) + P \cdot V + P \cdot V + P \cdot V >
\]

\[
= \frac{m}{3} \left( \sum_{i=1}^{n} \sum_{j=1}^{n} (\overline{F_{i,j}} \cdot \dot{v}_{i,j}) > + P \cdot V >
\]

(5)
\[ m \left< \sum_{i=1}^{n} \sum_{j=1}^{n} (\vec{F}_{ij} \cdot \vec{r}_{ij}) \right> + \left< \bar{P}V \right> + \frac{2}{3} \left< E_e \right> = 0 \] (6)

If the volume of the system \( V \) is constant, then:

\[
\bar{P} = \frac{2N}{3V} \left< E_e \right> + \frac{1}{3V} \left< \sum_{i,j} \vec{F}_{ij} \cdot \vec{r}_{ij} \right>
= \frac{1}{3V} \sum_{k=0}^{n} \sum_{i,j} m^i \nu_{\alpha} v_{\alpha}^i + \frac{1}{2} \sum_{i,j} f_{\alpha} f_{\alpha} f_{\alpha}
\] (7)

According to the derivation, the first term in the pressure formula (7) can be thought as the average value of particles’ thermal movement in per unit volume for the equilibrium molecular dynamics model, and the second one is a one-way force between particles in the system. In other words, the pressure of the system is balanced against the two parts. For periodic boundary conditions, the counter-pressure acting on the outside of the boundary only needs to calculate the correlation term of the internal particle. and the force from particles outside the system on the internal particles does not be considered.

For the second term in formula (7), there is another derivation \[^9\], which states that the pressure due to the interaction between the particles can be given by the pressure’s definition, in this article we call it as the second explanation, the force applied to the imaginary surface of the unit area is as follows:

\[
\bar{P}_{fs} = \frac{1}{AL} \int_0^1 \sum_{i,j} F_{ij} dx 
\] (8)

Where \( i \) and \( j \) are the particles located on different sides of the imaginary plane respectively. In order to simplify the integral formula into summation form, the length along the x direction is divided into \( n \) parts, where the length of each piece is \( \Delta x \), the integral formula can be simplified as

\[
\bar{P}_{fs} = \frac{1}{AL} \sum_{k=0}^{n} \sum_{i,j} F_{ij} \Delta x_{k+1} 
\] (9)

When we need to compute the pressure generated by the interaction between the particles \( i \) and \( j \), we only need to compute the partial intervals along the x direction between the \( i \) and \( j \) particles, and the formula can be further simplified:

\[
\bar{P}_{fs} = \frac{1}{AL} \sum_{i} \sum_{j} F_{ij} \Delta x_{j} 
\] (10)

At this point, \( i, j \) is still particles on different side of the hypothetical plane. While the range extending to the whole model space, the effect from particle \( i \) to \( j \) equal to the effect from \( j \) to \( i \), so the interaction between particles \( i \) and \( j \) can be calculated only once, the formula is simplified to:

\[
\bar{P}_{fs} = \frac{1}{AL} \sum_{i} \sum_{j} F_{ij} x_{ij} 
\] (11)

The expression in the form of ensemble is:

\[
\left< P_{fs} \right> = \frac{1}{V} \left< \sum_{i=1}^{n} \sum_{j=1}^{n} F_{ij} x_{ij} \right> 
\] (12)

For the simulation under periodic boundary conditions, the model is set as a system with an infinite loop. The particles on both sides of the periodic boundary are all simulated objects. Due to the limitation of the computer, the system is divided into two parts by the hypothetical boundary, inside and outside the boundary. According to the formula (12), computation of pressure not only requires the calculation of the intermolecular interactions, but the particle interactions between the two sides of the boundary should also be considered. Although the two different derivations of the Virial formula above lead to different understandings of the formulas, it is clear that the second derivation is more suitable for explaining the simulations under periodic boundary conditions than the first one. For the periodic boundary conditions, because the force to calculate the pressure does not only derive from the
internal objects, but also from the surrounding boundary particles, the formula can be further expressed as:

\[
P = \frac{1}{3V} \sum_{i=1}^{3} \sum_{j=1}^{n} m_{ij} v_{ij} v_{ij} + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij} f_{ij} + \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij} f_{ij} \geq 0
\]  \hspace{0.5cm} (13)

Where \( N \) is the number of the particles outside boundary, which have the effective interaction with particles inside the boundary, \( i \) and \( j \) are the particles inside the boundary.

It should be noted that during the calculation process, the ensemble average values of the pressure in all directions should be calculated respectively. With taking into account the isotropy for fluid pressure, the pressure in respective directions should use the absolute value to calculate the total pressure.

3. The relationship between model size and the pressure results for three-dimensional fluid

Lots of the pressure calculation results are used to analyze influencing factors in order to obtain the correct calculation condition. The fluid model used in this paper is the uniform liquid argon fluid model, NVT ensemble, periodic boundary conditions, there is no obvious interface between the model and the boundary particles, the potential is the commonly used LJ potential, the initial arrangement of argon atoms for the FCC structure, \( \sigma \) is taken as 0.341 nm, the time step as 1.E-14 seconds, the control temperature is 91.1K.

In this section, we discuss the pressure results with the same calculation range in different models. Length represents the side length of the calculation cube. Pressure is calculated respectively with different models as 7 × 7 × 7FCC, 8 × 8 × 8FCC, 9 × 9 × 9FCC and 10 × 10 × 10FCC for 50,000 steps. The results are shown as follows in Fig.1.

![Figure 1. The result of pressure with different models.](image)

From the results of Fig.1, we can see that the pressures calculation results are similar with the same calculation range even models are different, the relative fluctuations of pressure results do not exceed 8.94% under the same calculation range in different models. It can be concluded that the pressure calculation results are not marked difference with the calculation model itself, but mainly with the size of calculation range. It can also be further deduced that the pressure calculation result decays continuously with the increase of the calculation range, and the attenuation curve tends to be smooth and steady.

The conclusion is that the bigger the calculation range is not the better, because the pressure result is decaying continuously. The calculation condition of transport coefficients need refer to the simulation result of pressure which should be consistent with the experimental results.
Table 1. Pressure-length data for 10×10×10FCC.

| Length (nm) of calculation cube | 1.8 | 1.9 | 2 | 2.1 | 2.2 | 2.3 | 2.4 | 2.5 | 2.6 | 2.7 |
|-------------------------------|-----|-----|---|-----|-----|-----|-----|-----|-----|-----|
| Pressure×10^7 Pa              | 2.44| 2.28| 2.16| 2.06| 1.95| 1.85| 1.76| 1.68| 1.62| 1.54|

According to the experimental results[^11^], when the liquid argon density is 1.413g/cm^3^ and the temperature is at 91.1K, the pressure value should be 1.55E+7 Pa, then calculate range shown in Table 1 should be 2.7nm × 2.7nm × 2.7nm smaller, the minimum model to meet calculation range and the requirements of a sufficient border spacing is 9×9×9FCC.

4. Verify the viscosity simulation results referred to pressure calculation

The calculation of the viscosity with equilibrium molecular dynamics often uses the Green-Kubo formula which is based on the time self-correlation theory[^10^].

\[ \eta = \frac{V}{3k_BT} \int_0^t \sum_{\alpha, \beta} \left\{ \left( P_{\alpha\beta} (0) P_{\alpha\beta} (r) \right) \right\} \]  (14)

where

\[ P_{\alpha\beta} (r, \tau) = \frac{1}{T} \left[ \sum_{i=1}^n m_i v_{i\alpha} v_{i\beta} + \sum_{j=1}^n \sum_{j=1}^n \delta_{\alpha\beta} - \delta_{\alpha\beta} \right] \]  (15)

From the expression, we can see that \( P_{\alpha\beta} (r, \tau) \) is the shear stress in the direction of \( \alpha, \beta \) at the moment \( \tau \), that is, the viscosity calculation is based on the stress calculation. Therefore, the calculation condition of pressure can be referred to viscosity simulation, rationality of pressure calculation can also be verified by the result of shear viscosity.

The pressure results under different calculation range are shown in Table 1. From Figure 1 and Table 1, under the premise that the simulation results of pressure are in line with the experimental results, the models and control factors above are simulated and the calculation range is taken as the cube with a side length of 2.7 nm. The viscosity curve is obtained as shown in Fig.2, and the shear viscosity result is 2.32E-04 Pa·s, and the relative error between the experimental result 2.46E-04 Pa·s[^11^] is 5.7%.

![Viscous coefficient-time curve of Green-Kubo method](image)

5. Conclusions

By comparing the pressure results under different conditions, it can be drawn:
1. When using Virial formula of the equilibrium molecular dynamics method to calculate the pressure, it is necessary not only to consider the interaction between the particles inside the model, but also to consider the effect from the boundary particles.

2. In the case of periodic boundary conditions, the pressure curve may be imbalanced affected by the boundary conditions. To avoid this situation, the calculation space should be set at a position far away from the boundary layer, that is, the distance from the boundary layer is greater than the cut-off radius of the potential function and closer to the centre.

3. Pressure results are not affected by the model scale significantly but by the size of the calculation range and declines with the increase of the calculation range.

4. In order to obtain stable viscosity results closed to the experiment, the pressure simulation results should be referenced, that is, for viscosity calculation, the calculation of the scale and control factors should first meet the pressure simulation results in line with the experiment.

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