Molecular Simulation

The Virial of Angle Dependent Potentials in Molecular Dynamics Simulations

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THE VIRIAL OF ANGLE DEPENDENT POTENTIALS IN MOLECULAR DYNAMICS SIMULATIONS

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It is proved that the scalar virial of potentials that only depend on angles is zero. This is proved for nonperiodic boundary conditions as well as periodic boundary condition (PBC) systems. This theory is tested on an molecular dynamics simulation butane with PBC.

KEY WORDS: Angle dependent potentials, virial, pressure, molecular dynamics simulation.

1 INTRODUCTION

Since the pressure is an important observable property of molecular dynamics (M.D.) systems, in normal M.D. simulation practice the pressure of the system is calculated every time step. The pressure is calculated as the sum of a kinetic part and a configurational part, the *virial* [1]. The virial in its turn consists of contributions from different types of interactions as Lennard-Jones-, Coulomb-, bond-angle- and dihedral interactions. It is easily seen that the virial expression of central force interactions represents a force flux averaged over the system. However, angle dependent interactions are more complex, so understanding their contribution to the virial is less straightforward. In this article we will prove that the momentary scalar virial of angle dependent interactions is zero, and that the time averaged dimensional virial in isotropic systems is zero. We prove the first property three times: first in an informal way both for periodic boundary conditions (PBC) and non-PBC systems, then in a formal way for non-PBC systems, and finally in appendix A for PBC systems. To show the correctness of these theorems we present the results of an M.D. simulation of butane.

A practical implication of these findings is that, to prevent superfluous numerical noise with zero mean in the scalar virial, it should be calculated using only forces of non-angle-dependent interactions.

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2 THEORY

The momentary pressure tensor $\mathbf{P}$ of an N particle non-PBC M.D. system is a 3×3 matrix which is calculated as

$$\mathbf{P} = \frac{2}{V}(\mathbf{K} - \mathbf{W}) \tag{1}$$

with

$$\mathbf{K}_{\alpha\beta} \equiv \frac{1}{2} \sum_{i=1}^{N} m_i (\mathbf{v}_i)_\alpha (\mathbf{v}_i)_\beta \tag{2}$$

and

$$\mathbf{W}_{\alpha\beta} \equiv -\frac{1}{2} \sum_{i=1}^{N} (\mathbf{r}_i)_\alpha (\mathbf{F}_i)_\beta \tag{3}$$

and where $V \equiv box\ volume$, and $\mathbf{F}_i$ is the total force on particle i exerted by other particles (so not the wall) of the system. For M.D. systems with PBC (3) does not hold, so here we concentrate on non-PBC systems. PBC systems are treated in Appendix A.

The scalar pressure P is defined as

$$P \equiv \tfrac{1}{3} \operatorname{trace}(\mathbf{P}) \tag{4}$$

while the pressure per dimension is given by $\mathbf{P}_{xx}$, $\mathbf{P}_{yy}$ and $\mathbf{P}_{zz}$. Because we are interested in the virial contribution to the scalar pressure and to the pressure per dimension we define the scalar virial W as

$$W \equiv \tfrac{1}{3} \operatorname{trace}(\mathbf{W}) \tag{5}$$

The virial per dimension is given by $\mathbf{W}_{xx}$, $\mathbf{W}_{yy}$ and $\mathbf{W}_{zz}$.

2.1 The virial of interactions with angle dependent potentials

The class of angle dependent interactions consists of interactions for which the potential is invariant under translation, rotation, and uniform scaling of the system in all dimensions. The most commonly used interactions in this class are the bond-angle interaction, and the proper- and improper dihedral interaction. These interactions have in common that the potential is of the form $V \equiv V(\varphi)$ where $\cos \varphi$ is defined as an inner product between two unit vectors.

Let us consider a static system (that is a system without motion) with only angle dependent interactions. When we translate or rotate such a system or scale it in every dimension with the same factor $0 < \alpha < \infty$, the angles in the system do not change. This means that the internal energy U of the system does not change, i.e. $\Delta U = 0$. Using $\Delta U = P \cdot \Delta V$, we see that $P = 0$, where P is the scalar pressure of the system, and $\Delta V = (\alpha^3 - 1)V_0$ is the change in volume. From $P = 0$, using (4), (1), $\mathbf{K} = 0$, and (5) we find $W = 0$. This informal proof holds for non-PBC and PBC systems because scaling of a single system, and scaling of identical systems stacked in a space filling way, does not change any angle.

In the next paragraphs we will prove again that $W = 0$ for angle dependent interactions, but then in a formal way. We will concentrate on non-PBC systems. The proof for PBC systems is quite analogous but a bit more complex because then particles in image boxes have to be considered; it is given in appendix A.

We will prove again that $trace(\mathbf{W}) = 0$ for angle dependent interactions. Using definition (3) of $\mathbf{W}$, this is equivalent to proving

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = 0 \tag{6}$$

with $\mathbf{F}_i$ the total force on particle i by angle dependent interactions.

As a preliminary we will derive two properties about the angle defined by three particles. Three particles a, b, c define an angle ϕ, where ϕ is the angle between the lines a, b and b and c. Because ϕ is invariant under translation of the system a, b, c we have

$$\nabla_a \phi + \nabla_b \phi + \nabla_c \phi = 0. \tag{7}$$

The second property we want to derive is

$$\mathbf{r}_{ab} \cdot \nabla_a \phi = 0 \quad \text{and} \quad \mathbf{r}_{cb} \cdot \nabla_c \phi = 0. \tag{8}$$

We could prove this by giving a definition of ϕ and applying the due mathematical machinery to this. However, a much shorter proof can be given by an informal approach. $\nabla_a \phi \cdot d\mathbf{r}_a$ is the change in ϕ due to an infinitesimal change $d\mathbf{r}_a$ in the position of atom a. If $d\mathbf{r}_a$ is parallel to $\mathbf{r}_{ab}$ there is no change in ϕ and thus $\nabla_a \phi \cdot d\mathbf{r}_a = 0$. Therefore $\mathbf{r}_{ab} \cdot \nabla_a \phi = 0$ and analogously $\mathbf{r}_{cb} \cdot \nabla_c \phi = 0$.

Having done this groundwork we can start with the actual proof. We define the *shape* of a system of N particles as the set of geometrical quantities that do not change under translation, rotation, or scaling with a factor α of the system. The shape of a system is specified by giving a *complete set of independent angles* defined by particle triples. For three particles, two angles suffice to specify the shape. For every additional particle, three more angles are required. In general, $3N - 7 \equiv M$ angles are required for an $N \geqslant 3$ particle system.

Because every angle occurring in the system can be calculated from the complete set of independent angles, every angle dependent potential energy function V only depends on the complete set of independent angles, i.e. $V = V(\phi_1, \ldots, \phi_M)$.

Because we are interested in the scalar virial W of a system with only angle dependent potentials we want to calculate

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1}^{N} \mathbf{r}_i \cdot (-\nabla_i V) = \tag{9}$$

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \left(-\sum_{\gamma=1}^{M} \frac{dV}{d\phi_\gamma} (\nabla_i \phi_\gamma) \right) = -\sum_{\gamma=1}^{M} \left(\frac{dV}{d\phi_\gamma} \sum_{i=1}^{N} (\mathbf{r}_i \cdot \nabla_i \phi_\gamma) \right). \tag{10}$$

For a specific γ, ϕ_γ is a specific angle from the complete set of independent angles. This means that for fixed γ and i running through all particles, we get three non-zero values

for $\nabla_i \phi_\gamma$. That is because ϕ_γ is defined by three particles, say a, b, c. Using (7) and (8) we can write

$$\sum_{i=1}^{N} (\mathbf{r}_i \cdot \nabla_i \phi_\gamma) = \mathbf{r}_a \cdot \nabla_a \phi_\gamma + \mathbf{r}_b \cdot (-(\nabla_a + \nabla_c)\phi_\gamma) + \mathbf{r}_c \cdot \nabla_c \phi_\gamma = \tag{11}$$

$$\mathbf{r}_{ab} \cdot \nabla_a \phi_\gamma + \mathbf{r}_{cb} \cdot \nabla_c \phi = 0 \tag{12}$$

This means that the momentary scalar virial of angle dependent interactions is zero.

Using this result we can say something about the time averaged virial per dimension of angle dependent systems that are orientational diffusive, that is, systems in which individual molecules have no time averaged directional preference. We proved that the scalar virial, which is the sum of three virials per dimension, is zero. Because in every dimension of an isotropic system the scalar virial occurs with equal probability, *the time averaged virial per dimension will be zero*. Of course averaging should take place much longer than the orientational correlation time.

3 SIMULATED SYSTEM AND METHODS

In order to verify the above theoretical results molecular dynamics simulations have been performed using the program package Gromos [2]. A model system with PBC consisting of 64 butane-like molecules was chosen in order to have a simple system yet comprising internal degrees of freedom. Each molecule consisted of four atoms, i.e. the hydrogens were included in the carbons to form united atoms. The force field employed was the standard Gromos force field. It consists of a Lennard-Jones 6–12 potential for the non-bounded interactions between all atoms in different molecules and, with different parameters, between the end atoms of the same molecule. For angle interactions an harmonic bond angle potential was used

$$V(\theta) = C_\theta(\theta - \theta_0)^2 \tag{13}$$

where $\theta_0 (= 109.5°)$ is the equilibrium value of the angle θ. For dihedral interactions a periodic dihedral potential was used

$$V(\phi) = C_\phi(\cos(3\phi) + 1) \tag{14}$$

where ϕ is the dihedral angle defined such that $\phi = 0$ for a *cis* configuration. The parameters used for the angle-dependent and non-bonded potentials were the same as in the G simulation of [3]. The bond lengths b were represented by a harmonic potential

$$V(b) = C_b(b - b_0)^2/2 \tag{15}$$

where b_0 is the equilibrium bond length (0.153 nm) and C_b the force constant (334.7 MJ mol^{-1} nm^{-2}). The contributions to the virial from the different parts of the potential were calculated and summed separately (for more details see [4]). The simulation lasted for 261 ps of which the last 100 ps were analyzed for this work. The temperature was weakly coupled to an external bath [5] at 260 K with a coupling constant of 0.1 ps yielding a resulting temperature of 259.8 K. The cubic periodic box had a side of 2.1 nm and the time step was 0.5 fs.

4 SIMULATION RESULTS

The contributions to the pressure from different sources are given in Table I. The time correlation functions of the pressure contribution of angle dependent potentials are also given in Figure 1. From this it is clear that the contribution from the angle-dependent potentials to the instantaneous scalar pressure (or rather the trace of stress tensor) is zero in accordance with the above theorem. Also the time averaged contributions to the pressure per dimension due to angle dependent potentials is zero. These contributions are, however, only zero for an isotropic system after a simulation period long enough to average out the thermodynamic fluctuations (which could be rather large and long-lived for a small system as this). The fluctuations in the *scalar* virial from the angle dependent forces are zero whereas the fluctuations in the individual components are large. The results agree with the fact that the instantaneous fluctuations in the diagonal elements of the pressure tensor are anticorrelated with a correlation coefficient of -0.5.

To summarize, we conclude that there is no direct contribution from angle dependent potentials to the scalar virial or its fluctuations. For an isotropic system there is also

Table 1 Average pressure contributions in $kJ \cdot mol^{-1} \cdot nm^{-3}$ from different sources for a simulation of 64 flexible butane-like molecules. (The virial contributions are multiplied by -2 and divided by the volume and the kinetic contribution equals $\sum_i m_i v_i^2 / V$ in each direction). R.M.S. fluctuations are given in parenthesis.

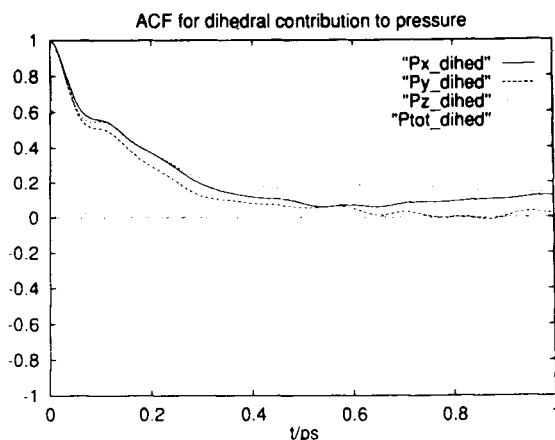|	Kinetic	L-J	Bonds	Angles	Dihedrals
P_{xx}	58.3(4.4)	11.3(21.2)	6.6(71.2)	$-0.41(18.25)$	0.01(2.09)
P_{yy}	61.2(4.5)	13.6(20.0)	6.3(75.9)	0.09(18.67)	$-0.15(2.04)$
P_{zz}	58.8(4.6)	10.2(19.9)	6.3(73.0)	0.32(18.92)	0.15(2.04)
P	59.5(1.6)	11.7(13.8)	6.4(50.3)	$-1 \times 10^{-6}(10^{-4})$	$-5 \times 10^{-8}(10^{-5})$

Figure 1 Time correlation function for the deviation from the average pressure for the contributions of the dihedral potential to the total pressure for the butane-like system. Dotted curve: scalar pressure P (average of diagonal elements); Solid curve: P_{xx}; Long dashed curve: P_{yy}; Short dashed curve: P_{zz}. Note that the correlation for the total pressure is zero after the first point (10 fs) of the correlation function indicating that the total pressure is just numerical noise.

no contribution to the average of the diagonal components of the pressure tensor but nevertheless there is a contribution to their fluctuations.

APPENDIX A

In M.D. simulations with PBC, particles in the central box interact with particles in the central box *and particles in image systems.* Because for non-bonded interactions a cut-off radius is used, and because generally the separation of particles involved in the same bonded interaction is less than the box size, only particles in boxes directly adjacent to the central box are involved in boundary crossing interactions. Therefore, in case of a tri-clinic box, we only have to consider particles in the central box and its 26 directly surround-ing boxes. Other box shapes may have less surrounding boxes, but otherwise may be treated as the triclinic box. Therefore, in the following we only consider a triclinic box.

We identify every box by a number k, with $-13 \leqslant k \leqslant 13$ in the following way. The central box has number 0. The box with number k is opposed, w.r.t. the central box, by box $-k$.

For a PBC system, a single particle number is not enough to identify a particle in a unique way. Therefore, particle i in box k is represents by $i.k$. So, $\mathbf{r}_{i.k}$ represents the position of particle i in box k, and $\mathbf{F}_{i.0,j.k}$ represents the force on particle i in the central box exerted by particle j in box k. For an interaction potential V, the force on particle $i.k$ is given by

$$\mathbf{F}_{i.k} = -\nabla_{i.k} V \qquad (A1)$$

where $i.k$ may lay in an image box.

For a non-PBC system the scalar virial W is calculated as

$$W \equiv -\frac{1}{2} \sum_{i=1}^{N} \mathbf{r}_{i.0} \cdot \mathbf{F}_{i.0} \qquad (A2)$$

In case of PBC, particles involved in interactions, notably bonded interactions, may lay in image systems. For virial calculations *the actual position* $\mathbf{r}_{i.k}$ *of every particle should be used.* So, (A2) then becomes

$$W \equiv -\frac{1}{2} \sum_{k=-13}^{13} \sum_{i=1}^{N} \mathbf{r}_{i.k} \cdot \mathbf{F}_{i.k} \qquad (A3)$$

For example, in Figure 2 V consists of a single dihedral interaction which crosses the border between box 0 and 1. In that case $\mathbf{F}_{i.k} = -\nabla_{i.k} V$ is non-zero for $i.k$ is 1.0, 2.0, 3.1 and 4.1. Of course an identical interaction exists which crosses the boundary between box 0 and box -1. In the following we assume that in the interaction potential of the whole system only one of every pair of boundary crossing interactions is included, which one does not matter.

For sake of completeness we want to mention that in case of PBC the force $\mathbf{F}_i$ which is used to calculate the new velocity of particle i is calculated as

$$\mathbf{F}_i = \sum_{k=-13}^{13} \mathbf{F}_{i.k} \qquad (A4)$$

i.e. the forces on all images of particle i, including the unshifted image, are summed. From $\mathbf{F}_i$ it can not be deduced which part of $\mathbf{F}_i$ results from which image of particle i, so $\mathbf{F}_i$ can not be used for the virial calculations. That is because for the virial calculation the constituting parts of $\mathbf{F}_i$, being the forces $\mathbf{F}_{i,k}$, and the respective positions $\mathbf{r}_{i,k}$ are required. For a more thorough introduction and use of this notation see [6].

Now that we have introduced a notation for particles and boxes in case of PBC we can start with the actual proof. It is analogous to the proof in section 2.1. We will use the letters a, b, c as particle numbers, and the letters k, l, m as box identifiers.

As a preliminary we will derive two properties about the angle defined by three particles of which some may be in image systems. Three particles $a.k$, $b.l$, $c.m$ define an angle ϕ, where ϕ is the angle between the lines $a.k$, $b.l$ and $b.l$, $c.m$. Because ϕ is invariant under translation of the system of particles $a.k$, $b.l$, $c.m$ we have

$$\nabla_{a.k}\phi + \nabla_{b.l}\phi + \nabla_{c.m}\phi = 0. \tag{A5}$$

The second property we want to derive is

$$\mathbf{r}_{a.k,b.l} \cdot \nabla_{a.k}\phi = 0 \quad \text{and} \quad \mathbf{r}_{c.m,b.l} \cdot \nabla_{c.m}\phi = 0. \tag{A6}$$

We prove this in an informal way. $\nabla_{a.k}\phi \cdot d\mathbf{r}_{a.k}$ is the change in ϕ due to an infinitesimal change $d\mathbf{r}_{a.k}$ in the position of atom $a.k$. If $d\mathbf{r}_{a.k}$ is parallel to $\mathbf{r}_{a.k,b.l}$ there is no change in ϕ and thus $\nabla_{a.k}\phi \cdot d\mathbf{r}_{a.k} = 0$. Therefore $\mathbf{r}_{a.k,b.l} \cdot \nabla_{a.k}\phi = 0$ and analogously $\mathbf{r}_{c.m,b.l} \cdot \nabla_{c.m}\phi = 0$.

The shape of a PBC system is specified by giving a *complete set of independent angles* defined by particle triples. We have to consider particles in the central box and particles in image systems so we have a total of $27\,N$ particles. Therefore, there are $3(27\,N) - 7 \equiv M$ independent angles in case of PBC. That the position of particle $i.k$ is related to the position of $i.0$ does not change this.

Because every angle occurring in the system of 27 boxes can be calculated from the complete set of independent angles, every angle dependent potential energy function V only depends on the complete set of independent angles, i.e. $V = V(\phi_1, \ldots, \phi_M)$.

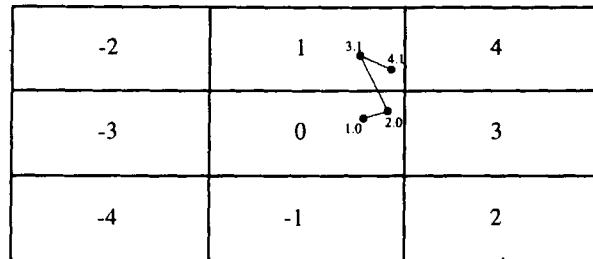| -2 | 1 | 4 |
| -3 | 0 | 3 |
| -4 | -1 | 2 |

Figure 2 PBC system with boundary crossing dihedral interaction. Particles are identified by giving their number and box number.

Because we are interested in the scalar virial W of a system with only angle dependent potentials we want to calculate

$$\sum_{i=1}^{N} \sum_{k=-13}^{13} \mathbf{r}_{i.k} \cdot \mathbf{F}_{i.k} = \sum_{i=1}^{N} \sum_{k=-13}^{13} \mathbf{r}_{i.k} \cdot (-\nabla_{i.k} V) = \qquad (A7)$$

$$\sum_{i=1}^{N} \sum_{k=-13}^{13} \mathbf{r}_{i.k} \cdot \left(-\sum_{\gamma=1}^{M} \frac{dV}{d\phi_\gamma} (\nabla_{i.k} \phi_\gamma) \right) = -\sum_{\gamma=1}^{M} \left(\frac{dV}{d\phi_\gamma} \sum_{i=1}^{N} \sum_{k=-13}^{13} (\mathbf{r}_{i.k} \cdot \nabla_{i.k} \phi_\gamma) \right). \quad (A8)$$

For a specific γ, ϕ_γ is a specific angle from the complete set of independent angles. This means that for fixed γ and $i.k$ running through all particles and all 27 boxes, we get three non-zero values for $\nabla_{i.k} \phi_\gamma$. That is because ϕ_γ is defined by three particles, say $a.k$, $b.l$, $c.m$. Using (A5) and (A6) we can write

$$\sum_{i=1}^{N} \sum_{k=-13}^{13} (\mathbf{r}_{i.k} \cdot \nabla_{i.k} \phi_\gamma) = \mathbf{r}_{a.k} \cdot \nabla_{a.k} \phi_\gamma + \mathbf{r}_{b.l} \cdot (-(\nabla_{a.k} + \nabla_{c.m}) \phi_\gamma) + \mathbf{r}_{c.m} \cdot \nabla_{c.m} \phi_\gamma = \quad (A9)$$

$$\mathbf{r}_{a.k,b.l} \cdot \nabla_{a.k} \phi_\gamma + \mathbf{r}_{c.m,b.l} \cdot \nabla_{c.m} \phi = 0 \qquad (A10)$$

This means that the momentary scalar virial of angle dependent interactions in a PBC system is zero. Analogous to section 2.1 it follows that the time averaged dimensional virial of an isotropic PBC system is zero.

Acknowledgement

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