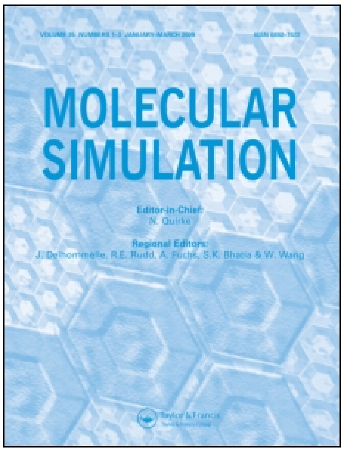

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On the Calculation of the Contribution to the Pressure of Angle-Dependent Potentials

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ON THE CALCULATION OF THE CONTRIBUTION TO THE PRESSURE OF ANGLE-DEPENDENT POTENTIALS

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This short paper clarifies the situation regarding the calculation of the contribution of angle-dependent potentials to the pressure. By comparing two derivations of the forces originating from an angle-bending potential on a system of three atoms joined by flexible or rigid bonds it is demonstrated that *in practice* it is not correct to assume that the contribution is always zero.

KEY WORDS: Pressure, angle-dependent potentials, molecular dynamics simulation, constraints.

1. INTRODUCTION

The purpose of this short note is to clarify the situation regarding the calculation of the contribution of angle-dependent potentials to the pressure. In a recent paper [1] a comprehensive scheme has been set out for the calculation of the 'atomic' pressure tensor **P** in three-dimensional fully periodic systems. In this paper (see section 3.3.2 of [1]) it was stated that *in practice* is was not necessarily correct to assume that purely angle-dependent potentials do not contribute to the scalar (or hydrostatic) pressure $p(=(P_{xx}+P_{yy}+P_{zz})/3)$ as has been previously argued [2–4]. Some care has to be exercised if rigidly constrained bonds connect atoms together and these constraints are used to simplify the algebra associated with the derivation of the forces.

In the next section two derivations of the pressure contribution of a bond-angle potential are made. The first assumes flexible bonds and is generally applicable and gives the expected net zero contribution result shown before [2–4]. The second is for the specific case where the bonds are defined to be rigid and leads to a nominal non-zero contribution. Some remarks follow in section 3.

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2. ANGLE-DEPENDENT POTENTIAL CONTRIBUTION TO THE PRESSURE

Let us consider a system of three particles at positions $(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ connected by two bonds. The cosine of the angle between them is

$$\cos(\theta) = \frac{(\mathbf{R}_1 - \mathbf{R}_2)\cdot(\mathbf{R}_3 - \mathbf{R}_2)}{(|\mathbf{R}_1 - \mathbf{R}_2||\mathbf{R}_3 - \mathbf{R}_2|)} = \frac{\mathbf{R}_{12}\cdot\mathbf{R}_{32}}{|\mathbf{R}_{12}||\mathbf{R}_{32}|} \tag{1}$$

For a bond-angle potential $\Phi(\theta)$, continuous and differentiable, the force on particle 1 is given by

$$\mathbf{F}_1 = \frac{-\partial\Phi(\theta)}{\partial\mathbf{R}_1} = \frac{-\partial\Phi(\theta)}{\partial\cos(\theta)}\frac{\partial\cos(\theta)}{\partial\mathbf{R}_1} = g(\theta)\frac{\partial\cos(\theta)}{\partial\mathbf{R}_1} \tag{2}$$

Assuming that the negative differential of $\Phi(\theta)$ with respect to $\cos(\theta)$ is straightforward, and given by $g(\theta)$, the problem reduces to deriving the differential of $\cos\theta$ with respect to $\mathbf{R}_1$

$$\frac{\partial\cos(\theta)}{\partial\mathbf{R}_1} = \frac{\partial\left\{\dfrac{\mathbf{R}_{12}\cdot\mathbf{R}_{32}}{|\mathbf{R}_{12}||\mathbf{R}_{32}|}\right\}}{\partial\mathbf{R}_1} \tag{3}$$

2.1 *General Case: Bonds Assumed to be Flexible*

In the general case Equation 3 can be written as

$$\frac{\partial\cos(\theta)}{\partial\mathbf{R}_1} = \frac{\dfrac{\partial\mathbf{R}_{12}}{\partial\mathbf{R}_1}\cdot\mathbf{R}_{32}}{|\mathbf{R}_{12}||\mathbf{R}_{32}|} + \frac{\mathbf{R}_{12}\cdot\mathbf{R}_{32}}{|\mathbf{R}_{32}|}\frac{\partial|\mathbf{R}_{12}|^{-1}}{\partial\mathbf{R}_1} \tag{4}$$

Performing this differential and substituting into Equation 2 gives

$$\mathbf{F}_1 = g(\theta)\frac{1}{|\mathbf{R}_{12}|}\left\{\frac{\mathbf{R}_{32}}{|\mathbf{R}_{32}|} - \cos(\theta)\frac{\mathbf{R}_{12}}{|\mathbf{R}_{12}|}\right\} \tag{5}$$

which is the force on particle 1 due to the angle bending potential.

In an analogous manner the forces can be obtained on the other sites,

$$\mathbf{F}_2 = -\frac{\partial\Phi(\theta)}{\partial\mathbf{R}_2} = -g(\theta)\left\{\frac{\mathbf{R}_{12}+\mathbf{R}_{32}}{|\mathbf{R}_{12}||\mathbf{R}_{32}|} - \cos(\theta)\left(\frac{\mathbf{R}_{32}}{|\mathbf{R}_{32}|^2} + \frac{\mathbf{R}_{12}}{|\mathbf{R}_{12}|^2}\right)\right\} \tag{6}$$

and

$$\mathbf{F}_3 = \frac{-\partial\Phi(\theta)}{\partial\mathbf{R}_3} = g(\theta)\frac{1}{|\mathbf{R}_{32}|}\left\{\frac{\mathbf{R}_{12}}{|\mathbf{R}_{12}|} - \cos(\theta)\frac{\mathbf{R}_{32}}{|\mathbf{R}_{32}|}\right\} \tag{7}$$

Now the contribution p_θ to the scalar pressure for a set of particles like this is [1]

$$3Vp_\theta = \mathbf{R}_1 \cdot \mathbf{F}_1 + \mathbf{R}_2 \cdot \mathbf{F}_2 + \mathbf{R}_3 \cdot \mathbf{F}_3 \tag{8}$$

where V is the volume of the MD box. Making use of the fact that the sum of the forces on the three particles from the bending potential is zero allows Equation 8 to be rewritten as

$$3Vp_\theta = \mathbf{R}_1 \cdot \mathbf{F}_1 + \mathbf{R}_2 \cdot (-\mathbf{F}_1 - \mathbf{F}_3) + \mathbf{R}_3 \cdot \mathbf{F}_3 = \mathbf{R}_{12} \cdot \mathbf{F}_1 + \mathbf{R}_{32} \cdot \mathbf{F}_3 \tag{9}$$

In this general treatment $\mathbf{F}_1$ is perpendicular to $\mathbf{R}_{12}$ and $\mathbf{F}_3$ is perpendicular to $\mathbf{R}_{32}$ so it follows immediately that p_θ is zero; as discussed in detail previously [2–4].

2.2 Specific Case: Bonds Assumed to be Rigid

Alternatively, and quite legitimately, for *rigid* bonds Equation 3 can be written as

$$\frac{\partial \cos(\theta)}{\partial \mathbf{R}_1} = \frac{\partial \left\{ \dfrac{\mathbf{R}_{12} \cdot \mathbf{R}_{32}}{b_{12} b_{32}} \right\}}{\partial \mathbf{R}_1} \tag{10}$$

where we use the fact that $|\mathbf{R}_{12}| = b_{12}$ and $|\mathbf{R}_{32}| = b_{32}$ are constant lengths; maintained constant by some appropriate algorithm in the actual MD simulation. This is much simpler to differentiate, and possibly computationally advantageous, and gives for the forces

$$\mathbf{F}_1 = g(\theta) \frac{\mathbf{R}_{32}}{b_{12} b_{32}} \tag{11}$$

$$\mathbf{F}_2 = \frac{-\partial \Phi(\theta)}{\partial \mathbf{R}_2} = -g(\theta) \frac{\mathbf{R}_{32} + \mathbf{R}_{12}}{b_{12} b_{32}} \tag{12}$$

$$\mathbf{F}_3 = \frac{-\partial \Phi(\theta)}{\partial \mathbf{R}_3} = g(\theta) \frac{\mathbf{R}_{12}}{b_{12} b_{32}} \tag{13}$$

In this case $\mathbf{F}_1$ is directed along $\mathbf{R}_{32}$ which isn't necessarily perpendicular to $\mathbf{R}_{12}$ and evaluating the contribution to the scalar pressure (Eq. 8) gives

$$3Vp_\theta = \mathbf{R}_{12} \cdot \mathbf{F}_1 + \mathbf{R}_{32} \cdot \mathbf{F}_3 = 2g(\theta)\cos(\theta) \tag{14}$$

a nominally non-zero result.

What has happened, of course, is that, in addition to the components perpendicular to the bonds, there are now components of the bending forces directed along the bonds. These additional components will be resisted by an extra (over that which would normally be there if we'd used the general solution, Eqs. 5–7) force of constraint along the bond, the magnitude of which cancels out the apparent contribution to the scalar pressure of the bending forces.

3. REMARKS

In practice then one has to be careful when calculating contributions to the scalar pressure. Attention has to be paid to the way in which the forces themselves are derived, not only for the example given above but also for other angle-dependent potentials, e.g. torsion-angle potentials. Furthermore it should be noted that for a calculation of the pressure tensor all forces must be considered. For example, it is not correct to assume [5] that because the contribution to the scalar pressure is zero that the individual contributions to P_{xx}, P_{yy}, and P_{zz} are also zero. Only the trace of the pressure tensor is invariant to orthogonal transformations (e.g. rotation of the coordinate system), whereas its individual diagonal elements are not.

One other interesting question that arises in the rigid bond case is which set of forces, Equations 5–7 or Equations 11–13, is computationally more advantageous? Equations 11–13 are simpler to calculate but it could be argued that for a Shake type algorithm they lead to greater destruction of the bond length constraints during the 'free-flight' phase on account of there components directed along the bonds and thus require more iterations in the constraint algorithm. Of course, both sets of forces are bound to lead to some further violation of the bond constraints on top of that caused by the inertial motion of the atoms and any other forces, e.g. intermolecular, in operation. It is unlikely then that there is going to be much difference in terms of the number of Shake iterations required but this point is worth further investigation.

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