Reply to ''Comment on 'Efficient stress relaxation in molecular dynamics simulations of semiflexible *n*-alkanes' ''

T. Mülders,[1] S. Toxvaerd,[2] and G. R. Kneller[1]
[1]*Centre de Biophysique Moléculaire, rue Charles Sadron, F-45071 Orléans, France*
[2]*Department of Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark*
(Received 4 February 2000; revised manuscript received 19 July 2000; published 23 January 2001)

The main issue of our original paper [Phys. Rev. E **58**, 6766 (1998)] is to demonstrate that the so-called atomic scaling, in which all available degrees of freedom are coupled to the pressure bath, is more efficient for stress relaxation in large molecules than the conventional molecular scaling in which the molecular centers of mass are coupled to the pressure bath, and internal degrees of freedom are left unchanged. Marchi and Procacci (MP) claim that this is not the case and try to demonstrate this by a simulation of the alkane system II (dotriacontanes, 32 monomers) treated in our paper, comparing atomic and molecular scaling with their R-RESPA integrator. They state that the stress-relaxation process should happen within a few picoseconds. As a possible explanation for their findings, they state an incorrect computation of the molecular pressure in our paper. Furthermore, MP claim there are further inconsistencies in our paper. In this Reply, it will be shown that contrary to the statements of MP, the virial has been computed correctly. Moreover, the inconsistency statement by MP results from the fact that MP have confused features in the figures of our paper. Finally, we do not agree that the stress relaxation of dotriacontanes seen in our simulations on the time scale of hundreds of picoseconds should happen within a few picoseconds. At room temperature, these systems form waxes and a slowing down of stress relaxation with respect to the liquid phase is to be expected. [S1063-651X(00)11412-6]

DOI: 10.1103/PhysRevE.63.028702 PACS number(s): 02.70.Ns, 31.15.Qg, 36.20.−r

The main issue of our original paper [1] is to demonstrate that the so-called atomic scaling, in which all available degrees of freedom are coupled to the pressure bath, is more efficient for stress relaxation in large molecules than the conventional molecular scaling. In the latter, only the molecular centers of mass are coupled to the pressure bath, and internal degrees of freedom are left unchanged. An important point in our approach (atomic scaling) is that geometrical constraints, such as fixed bond lengths, can be imposed while keeping a well-defined NPT ensemble. Marchi and Procacci (MP) claim that molecular scaling is as efficient as atomic scaling for stress relaxation. They try to demonstrate this by a simulation of the alkane system II (dotriacontanes, 32 monomers) treated in our paper, comparing atomic and molecular scaling with their R-RESPA integrator. They use a completely flexible alkane model and see an almost instantaneous stress relaxation (within a few picoseconds) for both scaling schemes. As a possible explanation for their findings, they state an incorrect computation of the molecular virial in our paper. Furthermore, MP claim there are further inconsistencies in our paper. In this Reply, it will be shown that, contrary to the statements of MP, we believe that the virial has been computed correctly. Moreover, the inconsistency statement by MP results from the fact that MP have confused features in the figures of our paper. Finally, we do not agree that the stress relaxation of dotriacontanes seen in our simulations on the time scale of hundreds of picoseconds should happen within a few picoseconds. At room temperature, these systems form waxes and a slowing down of stress relaxation with respect to the liquid phase is to be expected.

MP claim that the formula we use to compute the molecular pressure—formula (1) in the Comment (for a derivation, see the Appendix here in or [2])—is incorrect for long molecules whose lengths exceed half of the simulation box length. The reason quoted is that due to periodic boundary conditions, some intramolecular interactions become effectively *inter*molecular interactions between image molecules and should not be excluded from the summation in the virial. The exclusion concerns all *intra*molecular interactions. It is, however, irrelevant as to whether intramolecular forces are excluded or not, as long as they sum up to zero for each molecule (see the Appendix). This is, for instance, the case for any distance-dependent pair force (other forces need not be considered in this context). If one works with periodic boundary conditions, i.e., with a periodic potential, the pair forces are simply replaced by effective pair forces, irrespective of the range of the potential. An example is the Wigner potential describing Coulomb interactions in a cubic crystal. The Lennard-Jones forces under consideration here are, of course, short-ranged, but the principle is the same. Therefore, the total intramolecular force on a molecule treated with periodic boundary conditions is also zero, and the ''exclusion prime'' in the virial sum in Eq. (1) of the Comment is irrelevant. Another argument indicating that the intramolecular forces *must* sum up to zero follows from the conservation of the total momentum of the system. Any nonzero contribution to the total force onto a molecule arising from intramolecular interactions would violate the conservation of the system's total momentum. Clearly, this would be a nonphysical consequence.

MP assert that in our paper two different values for the volumes of the long alkane chains have been reported, i.e., that the volume corresponding to the simulation with molecular scaling is larger than the atomic scaling volume. However, the reported volumes (molecular scaling 65.01 ± 0.32 nm^3, atomic scaling 65.47 ± 0.35 nm^3) should rather be termed ''equal within the error bars.'' However, even the small difference could be understood as a conse-

quence of the enhanced stress relaxation for atomic scaling. This could lead to a slightly accelerated volume relaxation from the starting volume ($67.28\ \mathrm{nm}^3$). Furthermore, MP state in this context that the reported volume values are ''clearly inconsistent'' with Fig. 7 in our paper [1]. In this figure, the atomic pressure as well as the molecular pressure are depicted as both being computed during the *same* simulation with molecular scaling. Here the molecular pressure is the ''active'' dynamical variable, giving a feedback to the barostat, whereas the atomic pressure is a ''passive'' variable that is just computed for information. The analog for the atomic scaling simulation is shown in Fig. 8. Here the active variable is the atomic pressure and the passive variable is the molecular pressure. In contrast to the molecular scaling simulation (Fig. 7), the atomic and molecular pressure coincides at the end of the atomic scaling simulation (Fig. 8). This is an important result indicating that local equilibrium has been reached in the simulation with atomic scaling (Fig. 8) but not in the simulation using molecular scaling. MP have obviously confused which curve in which plot belongs to which simulation. They even claim that in our *atomic* scaling simulation, the volume should expand and not contract. The reason given is that the atomic pressure shown in Fig. 7 is higher than the external pressure of 1 atm. Marchi and Procacci have simply confused features in the figures, although these are clearly described. Figure 7 shows the atomic pressure during a *molecular scaling* simulation and has nothing to do with the *atomic scaling* simulation for which the corresponding pressures are shown in Fig. 8, but not in Fig. 7. Therefore, the conclusion given by MP that ''this is a further clue indicating that flawed computation might be playing a significant role in the MTK main results'' is invalid.

MP assert that one of the conclusions of our paper has been that ''the faster relaxation of constant pressure molecular dynamics simulations based on atomic scaling is responsible for differences in the computed thermodynamic observables if compared to molecular scaling.'' This is not true. Our paper suggests that the relaxation to equilibrium is accelerated when atomic scaling is used. Clearly, when an NPT equlibrium situation is reached, both methods (atomic and molecular scaling) must produce equal averages. We have mentioned this several times in our paper, in particular when discussing Figs. 7 and 8 (see discussion above).

The figures shown by MP are based on simulations with a different force field from the one used by us. Before discussing differences of 4% in the final volume, MP should have considered this point. Although MP claim that similar results are obtained when their force-field parameters are adjusted to reproduce the force field used by us, they neither show a plot nor do they report the final volume values corresponding to these adjusted parameters. It should also be kept in mind that MP do not use bond constraints in their simulations, as we did, but consider totally flexible molecules. In comparison with our method, they should have examined whether and how much stress is relaxed into the bond vibrations. The degrees of freedom are obviously not available in the semiflexible alkane models used in our simulations and could lead to an acceleration of stress relaxation.

However, all this does still not explain the extremely rapid stress relaxation in the picosecond range obtained by MP when compared to the slow relaxation of stress lasting (at least) hundreds of picoseconds in our paper. We note in this context that the long chain alkane system (dotriacontane) forms a paraffin, i.e., a wax, but not a liquid, under the simulation conditions ($P=1$ atm, $T=303$ K). The melting temperature of the dotriacontanes is 343 K [3]. Thus, we find that the order of magnitude of the relaxation rates that have been observed by us is to be expected. We are surprised about the fast liquid like relaxation observed by Marchi and Procacci. In waxlike alkane systems, an almost instantaneous stress relaxation, as observed by MP, is nonphysical. In order to convince ourselves that the simulated dynamics is realistic, we compared the frequency of breathing modes seen for the long alkane chains with results obtained from inelastic neutron-scattering experiments and found very good agreement. In contrast, MP do not show any comparison with experimental data. It would be interesting to see whether they find the same breathing modes, which would have been a demonstration that these motions are not quenched due to a fast but nonphysical volume relaxation.

APPENDIX

In this appendix, we show how the molecular virial $\Sigma_\gamma \mathbf{R}_\gamma \cdot \mathbf{F}_\gamma$ can be uniquely computed in a simulation employing atomic periodic boundary conditions, i.e., in a situation where atoms but not molecules are considered ''indivisible.'' In the following, N molecules are considered that are labeled with greek indices $\gamma, \delta, \ldots$, such that $\mathbf{R}_\gamma$ and $\mathbf{F}_\gamma$ denote the center-of-mass position of molecule γ and the total force on it, respectively. Each molecule contains n atoms and the notation $\mathbf{r}_{i_\gamma}$ refers to the position vector of atom $i_\gamma (i_\gamma = 1, \ldots, n)$ in molecule γ and $\mathbf{f}_{i_\gamma}$ is the force acting on this atom.

The following derivation is nearly identical to the one by Ferrario in [2]. We restrict ourselves to pairwise interaction potentials. The principal idea is to decompose the molecular virial $\Sigma_\gamma \mathbf{R}_\gamma \cdot \mathbf{F}_\gamma$ into different terms, which can be evaluated in a nonambiguous way in the presence of atomic periodic boundary conditions,

$$\begin{aligned}
\sum_{\gamma=1}^{N} \mathbf{R}_\gamma \cdot \mathbf{F}_\gamma &= \sum_{\gamma=1}^{N} \mathbf{R}_\gamma \cdot \underbrace{\sum_{i_\gamma=1}^{n} \mathbf{f}_{i_\gamma}}_{\mathbf{F}_\gamma} \\
&= \sum_{\gamma=1}^{N} \mathbf{R}_\gamma \cdot \sum_{i_\gamma=1}^{n} \sum_{\substack{\delta=1 \\ \delta\neq\gamma}}^{N} \sum_{j_\delta=1}^{n} \mathbf{f}_{i_\gamma j_\delta} \\
&= \sum_{\substack{\gamma,\delta=1 \\ \delta\neq\gamma}}^{N} \sum_{i_\gamma=1}^{n} \sum_{j_\delta=1}^{n} \mathbf{R}_\gamma \cdot \mathbf{f}_{i_\gamma j_\delta} \\
&= \sum_{\substack{\gamma,\delta=1 \\ \delta>\gamma}}^{N} \sum_{i_\gamma=1}^{n} \sum_{j_\delta=1}^{n} (\mathbf{R}_\gamma - \mathbf{R}_\delta) \cdot \mathbf{f}_{i_\gamma j_\delta}.
\end{aligned} \tag{A1}$$

Here $\mathbf{f}_{i_\gamma j_\delta}$ denotes the forces on atom i_γ due to the interaction with atom j_δ. These pair forces obey Newton's third law $\mathbf{f}_{i_\gamma j_\delta}=-\mathbf{f}_{j_\delta i_\gamma}$ which has been used to obtain the last equality. Use has been made of the fact that intramolecular forces do not contribute to the total force on molecule γ, explicitly $\Sigma_{i_\gamma=1}^{n}\Sigma_{j_\gamma=1}^{n}\mathbf{f}_{i_\gamma j_\gamma}=0$. Even for a periodic potential this remains true, the only difference being that the potential has to be replaced by an effective potential containing contributions from all images.

Introducing relative coordinates $\tilde{\mathbf{r}}_{i_\gamma}\equiv\mathbf{r}_{i_\gamma}-\mathbf{R}_\gamma$ allows the molecular virial to be rewritten as

$$\sum_{\gamma=1}^{N}\mathbf{R}_\gamma\cdot\mathbf{F}_\gamma=\sum_{\substack{\gamma,\delta=1\\ \delta>\gamma}}^{N}\sum_{i_\gamma=1}^{n}\sum_{j_\delta=1}^{n}[\mathbf{r}_{i_\gamma}-\mathbf{r}_{j_\delta}-(\tilde{\mathbf{r}}_{i_\gamma}-\tilde{\mathbf{r}}_{j_\delta})]\cdot\mathbf{f}_{i_\gamma j_\delta}. \tag{A2}$$

This last form of the molecular virial allows its evaluation to be done unambigiously when atomic periodic boundary conditions are used. Interpreting the interatomic distance vector $\mathbf{r}_{i_\gamma j_\delta}\equiv\mathbf{r}_{i_\gamma}-\mathbf{r}_{j_\delta}$ as its *minimum image* distance vector $\mathbf{r}^{\mathrm{NI}}_{i_\gamma j_\delta}$ (where NI stands for *nearest image*) gives the final expression for the molecular virial that can be uniquely evaluated during a simulation using atomic periodic boundaries:

$$\sum_{\gamma=1}^{N}\mathbf{R}_\gamma\cdot\mathbf{F}_\gamma=\sum_{\substack{\gamma,\delta=1\\ \delta>\gamma}}^{N}\sum_{i_\gamma=1}^{n}\sum_{j_\delta=1}^{n}(\mathbf{r}^{\mathrm{NI}}_{i_\gamma j_\delta}-\tilde{\mathbf{r}}_{i_\gamma}+\tilde{\mathbf{r}}_{j_\delta})\cdot\mathbf{f}_{i_\gamma j_\delta}. \tag{A3}$$

It has to be stressed that the summation over molecules runs over all $N(N-1)/2$ pairs of *different* molecules. This is exactly the expression we used when summing over all pairs of atoms which are in *different* molecules. Intramolecular interactions need not be included as long as they sum up to zero.

It is also worth mentioning that other expressions for the molecular virial are in use that do not follow the idea of transforming $\Sigma_\gamma\mathbf{R}_\gamma\cdot\mathbf{F}_\gamma$ in such a way that it can be uniquely determined in a simulation with atomic periodic boundaries [4]. In the context of the molecular version of the Nosé-Andersen simulation scheme, these alternate expressions, however, need not be considered because it is exactly the term $\Sigma_\gamma\mathbf{R}_\gamma\cdot\mathbf{F}_\gamma$ that appears in the equations of motion and that has to be computed. Therefore, it suffices to transform $\Sigma_\gamma\mathbf{R}_\gamma\cdot\mathbf{F}_\gamma$ such that it can be uniquely evaluated in a simulation with atomic periodic boundaries.

[1] T. Mülders, S. Toxvared, and G.R. Kneller, Phys. Rev. E **58**, 6766 (1998).

[2] M. Ferrario, in *Computer Simulation in Chemical Physics*, edited by M.P. Allen and D.J. Tildesley, Vol. 153 of *NATO Advanced Study Institute Series B: Physics* (Kluwer Academic Publishers, Dordrecht, 1993), pp. 153–171.

[3] *CRC Handbook of Chemistry and Physics*, 80th ed. CRC Press, Boca Raton, FL, 1999), Sec. 3, p. 149.

[4] D.N. Theodoru, T.D. Boone, L.R. Dodd, and K.F. Mansfield, Makromol. Chem., Theory Simul. **2**, 191 (1993).