Communications to the Editor

Comment on "Molecular Modeling of Polymers. 7. Ab Initio Demonstration of Torsional Angle Cooperativity in Linear Chains by Molecular Dynamics" by D. C. Doherty and A. J. Hopfinger (*Macromolecules* 1990, *23*, 676–678)

It is the aim of the authors, as can be deduced from their introduction and conclusions, to show the ab initio existence of torsion angle cooperativity in alkanes and its possible relevance with respect to structural phase transitions. Though the authors note that full details of the molecular dynamics simulations will be given later, we nevertheless feel it necessary to express our concern about these results, a view we will now support by the following arguments.

The terminology "ab initio" should be (and usually is) preserved for a first principles approach based on quantum mechanics. A molecular dynamics simulation involving an empirical force field such as MM2 in the present paper and simulating a phase transition by a static increase of a parameter (distance) at constant temperature should not be regarded as at the "ab initio" level.

The time scale of the simulations is rather confusing. It is first suggested that a 5-ps simulation has been carried out for six microstructures. Later it is stated that parts a and b of Figure 1 show correlation functions over the entire 30-ps trajectory. If the 30 ps is correct, the correlation function is a sum over the orthorhombic phase, the hexagonal phase, and the other four microstates in between and therefore has no sensible physical interpretation. Moreover, the time axis of parts a and b of Figure 1 only ranges from 0 to 2 ps. We *assume* the latter range being correct while the 3–5-ps range has been omitted because the numerical value of the correlation function has almost vanished.

The temperature at which the simulations have been carried out, $T = 305$ K, is not brought into connection with experimental data on C_{21} alkane crystals. We expect at least that the orthorhombic–hexagonal phase transition has been observed at that temperature, eventually under pressure.

According to the authors, Figure 2, showing a digitized representation of trajectories of adjacent torsional angles versus time over the time span 0–2.5 ps, illustrates their most important conclusion, i.e., the cooperativity of (1,3)-torsional angle pairs. First, there are only a few diagonals in this time span that show any "cooperative" behavior. Particularly, the second part from 1.3–2.5 ps looks entirely random. It is not clear why the authors have left out the range 2.5–5.0 ps if there were any noticeable diagonals to be seen in that range. It thus seems that at longer times there is no sign of cooperativity. Moreover, no quantification of the equilibration time has been given. Whenever there are modes that have a time constant on the picosecond scale, the equilibration time should *at least* surpass this value, i.e., lie in the range 5–10 ps. Since the simulation was said to take 5 ps per microstructure only, it is doubted whether the equilibration time is 5–10 ps (it is unusual that the true dynamics simulation time is shorter than the equilibration time). For these reasons we think that the "observed" torsional cooperativity in Figure 2 is highly questionable without any further information on the present simulation and without further simulation that shows the cooperativity repeatedly in time.

Doherty and Hopfinger say they expect that the cooperative motion of the torsional angles may be a very important factor in the structural phase transitions in these materials (solid alkanes). However, an ordinary acoustical mode might cause the behavior as revealed from the 0.6–1.0-ps time span in Figure 2. The value of 1 ps for the correlation time as given by Doherty and Hopfinger corresponds to a wavenumber of 30 cm^{-1}, which is in the range where acoustic (LA and TA) modes are usually observed in an alkane of the present length, i.e., C_{21}. Furthermore, it is well-known that a structural phase transition is accompanied by the appearance of a soft mode, the eigenvector of which describes the kind of structural change. This soft mode, the softer it becomes, is a collective mode. As a consequence, cooperativity is a well-known phenomenon in structural phase transitions. On the other hand, if it turns out, and this should be easily verifiable when both initial and final structures are known, that the torsional angle cooperativity is not connected to the structural phase transition, it is either an artifact (of equilibration or otherwise), an accidentally occurring phenomenon, or a well-defined excitation (TA mode) not particularly connected to and not inducing the phase transition.

Robert J. Meier

DSM Research, P.O. Box 18, 6160 MD Geleen
The Netherlands

Received December 13, 1990

0024-9297/91/2224-1692$02.50/0