

## Comment on “Adaptive Multiscale Molecular Dynamics of Macromolecular Fluids”

In a recent Letter, Nielsen, Moore, and Ensing [1] presented an “energy-conserving” adaptive resolution method for coupling different molecular representations. We here comment only on their basic simulation concept. We show that the algorithm, as described in the text, does not conserve thermodynamic equilibrium and will produce a significant energy drift. To couple an atomistic and coarse-grained region, Nielsen, Moore, and Ensing introduce a healing region with a space-dependent interpolation of the atomistic and coarse-grained potential energies, Eq. (2) of [1]. To this potential they add a term, Eq. (3), which should compensate the drift introduced by the interpolated potentials. This energy, though specified as unphysical, is claimed to control the thermodynamic stability as the central ingredient of their approach. The authors then claim that, as a result of the additional potential, the intermolecular force acting between two molecules is reduced to the space-dependent interpolation of the atomistic and coarse-grained one.

As we will show, the force interpolation cannot be derived from the potential proposed and the corresponding energy is a meaningless quantity, which does not preserve thermodynamic equilibrium. Other approaches also use a force interpolation scheme; however, they resort to a thermostat in the healing region to guarantee thermodynamic equilibrium [2,3]. If forces could be derived from the sum of the potentials of Eqs. (2) and (3), one could perform adaptive molecular dynamics simulations in the microcanonical ensemble. Thermodynamic equilibrium of the whole system should not require any additional coupling to external sources. It actually has been shown analytically that this is not possible [4,5].

We illustrate this by a simple numerical example. Consider a system composed of spherical particles which by crossing the healing region transform from representation *A* in one region of space into representation *B* in another region of space and vice versa. Note that the choice of the simple spherical molecules avoids any complication regarding the reintroduction of extra degrees of freedom (DOFs). Thus kinetic energy and (according to [1]) the potential energy are well defined. In simple words, we have tested the very meaning of the interpolation formula as derived in [1] for two different molecular representations. The two spherical potentials are derived from coarse graining a tetrahedral molecule [2] at two different thermodynamical state points of the reference liquid of tetrahedral molecules. The model systems *A* and *B* are carefully chosen, so that their equations of state coincide at the state point considered here:  $\rho = 0.0875$ ,  $T = 1.0$ , and  $P = 0.28$  in the reduced units of Ref. [2]. Thus in both regions their density naturally is the same and we start the simulation from a globally equilibrated configuration.

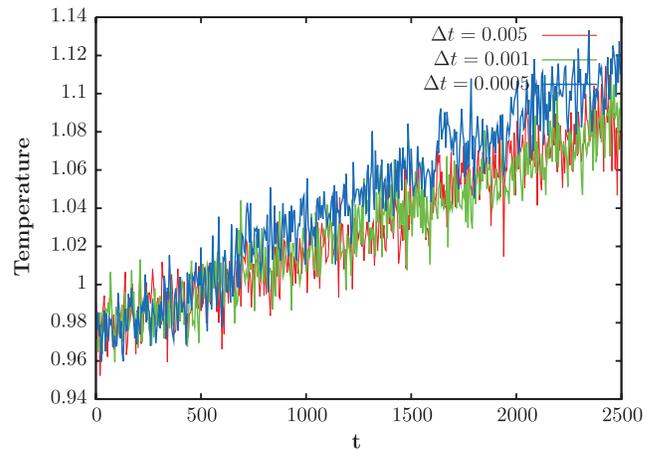


FIG. 1 (color). Temperature as a function of time for different integration time steps, in reduced units as in Ref. [2].

If the method of Ref. [1] worked as claimed, there should be no temperature drift during a standard *NVE* simulation using their claimed simulation setup (up to a minute time-step-dependent drift coming from numerical errors of the integration). Instead, Fig. 1 shows a strong temperature drift. The system is not in thermodynamic equilibrium, demonstrating that the protocol proposed by Nielsen, Moore, and Ensing cannot assure thermodynamic equilibrium, in agreement with analytical arguments [4].

In contrast, as shown for the adaptive resolution scheme method [2] (Ref. [9] of [1]), thermodynamic equilibrium can be controlled *only* by coupling the system to an external field and/or to a local thermostat [7]. That the “book-keeping energy” is meaningless was stated already by other authors [8]. For the case where DOFs also must be reinserted (or removed) in the healing region, the extra heat given by the thermostat for this process can be quantified *a posteriori* via the concept of fractional DOFs [7]. Moreover, the role of the thermostat as the only crucial tool to reintroduce DOFs has been clearly demonstrated in Ref. [9], where the reduction (or reinsertion) of 117 DOFs per molecule was performed.

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