Three-body potential for simulating bond swaps in molecular dynamics

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Tips and Tricks

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Abstract. Novel soft matter materials join the resistance of a permanent mesh of strong inter-particle bonds with the self-healing and restructuring properties allowed by bond-swapping processes. Theoretical and numerical studies of the dynamics of coarse-grained models of covalent adaptable networks and vitrimers require effective algorithms for modelling the corresponding evolution of the network topology. Here I propose a simple trick for performing molecular dynamics simulations of bond-swapping network systems with particle-level description. The method is based on the addition of a computationally non-expensive three-body repulsive potential that encodes for the single-bond per particle condition and establishes a flat potential energy surface for the bond swap.

1 Introduction

There is a significant ongoing effort in the direction of developing new classes of materials combining mechanical properties with self-healing, recycling and responsiveness properties. In the last years, an innovative class of polymeric materials has been synthesized [1–4]. Differently from thermosets, which are made of permanently cross-linked polymers, these new plastics consist of a covalent network that can rearrange its topology via a bond-switching mechanism, preserving the total number of bonds [5]. In these polymeric systems, the network is composed of persistent bonds that provide the rigidity typical of plastics. At the same time, the bond-switching mechanism allows for the release of internal stresses and for fracture healing. These dynamic covalent networks (DCN) (or covalent adaptable network) [6–8] will definitively provide in the near future a viable alternative to the present permanently linked polymeric materials. The systems presented in refs. [1–3] have been named vitrimers, since the viscosity follows an Arrhenius law, falling into the category of strong glass formers [9]. Just like silica glasses, they can be heated and reworked to take any new shape without dissolving. The interest in finding methods to model bond switching is not limited to vitrimers or DCN. Along the lines of using DNA as a material [10,11], a recent theoretical study has proposed a dynamic network entirely made of DNA sequences [12]. The bond-switching in such DNA gel is based on the toehold-mediated displacement [13], one of the basic processes exploited in dynamic DNA nanotechnology. Bond swapping has been also encoded in the design of stimulus-sensitive colloidal walkers [14] and in the design of DNA gels that melt on cooling [15]. Bond switching has also been proposed in the past as the mechanism controlling dynamics in atomic and molecular systems with strong directional interactions [16–18].

The theoretical investigation of these new classes of soft-matter materials requires the development of algorithms implementing bond swapping in coarse-grained models. The early numerical studies [5,19] have faced the problem of encoding in the Monte Carlo (MC) or in the Molecular Dynamics (MD) algorithm the possibility to swap bonds, when an unreacted free end finds itself close to an existing bond. The proposed solutions have been based on a stochastic selection between preserving the old bond or substituting it with the new one. The swap can be accepted with a finite probability, encoding the desired swap rate. The implementation of a stochastic event can be easily included in MC and in event-driven MD [5], but can hardly be incorporated in a standard MD without violating continuity in the potential energy and in the force. In this Tip and Tricks I propose a novel method that allows for bond swapping in standard MD. The method, in use in a currently ongoing project focused on the collective dynamics in models for vitrimers, can be readily applied to all continuous bonding pairwise potentials, which are able to generate network structures with well-defined bonds, without significantly altering the thermodynamic of the model. An additional parameter makes it possible to control the energetic barrier for swapping, going from the non-swapping case to the freely swapping one, adding the opportunity to investigate the cross-over from physical to chemical gels.

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The interaction energy of a bonded pair is described generically by a potential $V_{\text{bond}}(r)$ of arbitrary shape, acting between specific bonding sites of the particles, such that r is the site-site distance. r can in principle also indicate the distance between the centres of interacting atoms in a complex molecule. $V_{\text{bond}}(r)$ is usually characterised by a narrow minimum of depth ϵ around the bond distance $r_{\min}$ (*i.e.*, $\epsilon \equiv |V_{\text{bond}}(r_{\min})|$) and it vanishes beyond a properly defined cutoff r_{cutoff}. Thus, two particles are considered bonded if their relative distance is less than r_{cutoff}.

The basic idea of the method consists in the addition to the system potential energy of a repulsive three-body potential $V_{\text{threebody}}$ defined as

$$V_{\text{threebody}} = \lambda \sum_{ijk} \epsilon V_3(r_{ij}) V_3(r_{ik}), \qquad (1)$$

where the sum runs over all triples of bonded particles (particle i bonded both with k and j). r_{ij} is the distance between particle i and j and λ is a parameter that can be tuned to interpolate between the limits of swapping ($\lambda = 1$) and non-swapping ($\lambda \gg 1$) bonds. The pair potential $V_3(r)$ is defined as

$$V_3(r) = \begin{cases} 1, & r \leq r_{\min}, \\ \dfrac{-V_{\text{bond}}(r)}{\epsilon}, & r_{\min} \leq r \leq r_{\text{cutoff}}. \end{cases} \qquad (2)$$

The evaluation of the three-body potential does not require significant computational resources since it is defined in term of previously calculated quantities. Differently from the famous Stillinger-Weber potential [20], which favours the formation of a tetrahedral ordering via an angular dependence, here the three-body potential involves r_{ij} and r_{ik}, but does not depend on r_{jk}. Note that by construction $0 < V_{\text{threebody}} < \lambda\epsilon$, *i.e.* $V_{\text{threebody}}$ is a repulsive potential whose amplitude (in units of ϵ) can be externally controlled by the choice of the parameter λ. For large values of λ the three-body potential prevents the swap of any bond, offering the possibility to simulate even networks with infinite bond lifetime. When $\lambda = 1$ instead the three-body potential compensates the additional energy gain associated to the formation of a double bond and hence it creates an almost flat bonding hypersurface allowing for bond swapping in the absence of any activation energy. Indeed, ideally, an efficient bond swap should not require any change in the system potential energy such that, even at temperatures much smaller than the bond energy scale ϵ, the swap process can spontaneously take place. Swapping of covalent bonds, whose bond energy is significantly larger than the thermal energy, is a typical case.

Figure 1(a) shows a possible radial dependence of $V_{\text{bond}}(r)$ and the associated $V_3(r)$ (eq. (2)). The plot clearly shows how the repulsive $V_3(r)$ compensates for $V_{\text{bond}}(r)$. To better visualize how the three-body potential acts, consider a bonded pair and its collision with an incoming particle. When the incoming particle is further than r_{cutoff} the potential energy of the system composed
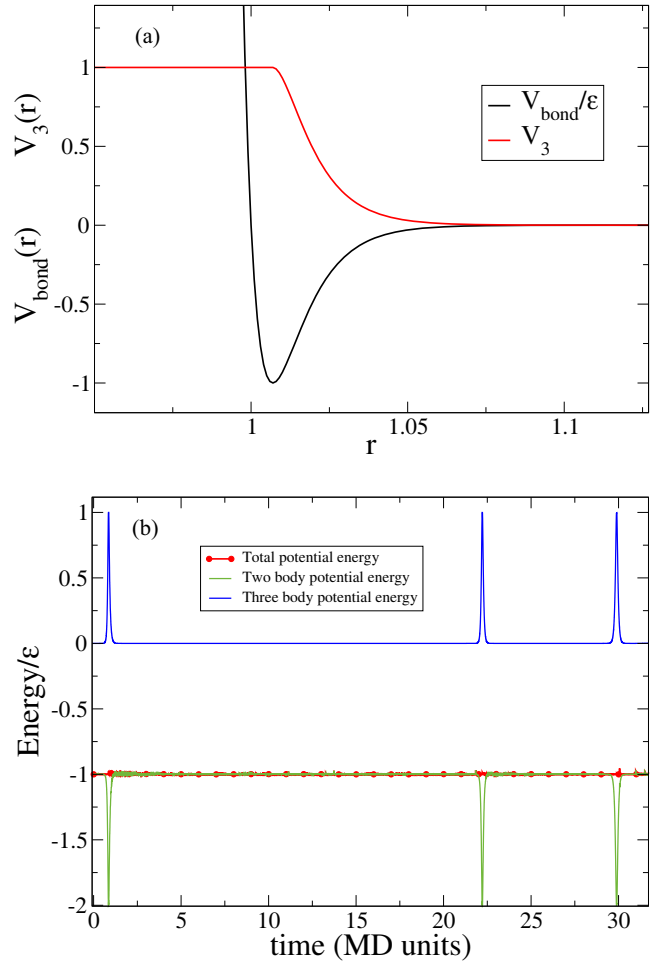

Fig. 1. (a) Radial dependence of a (normalized) typical bond potential ($V_{\text{bond}}(r)/\epsilon$) and of the associated $V_3(r)$ potential. For $r > r_{\min}$ the two potentials are opposite ($V_{\text{bond}}(r)/\epsilon = -V_3(r)$). (b) Time dependence of the potential energy in a system with only one bond. Three different swapping processes are observable. Note how the variation in two-body energy is compensated by the simultaneous variation of the three-body potential energy resulting in a flat potential energy surface for the swap process. Time is measured in MD units ($\sqrt{m\sigma^2/\epsilon}$).

by these three particles is $\approx -\epsilon$. When the incoming particle enters in the bonding volume of only one of the two particles forming the pair, the two-body component of the potential energy goes down to $\approx -2\epsilon$. Simultaneously the three-body interaction $\approx \lambda\epsilon$ sets in. In this way, when $\lambda = 1$, the potential energy of the three particles does not significantly change. Figure 1(b) shows the dependence of the different contributions to the potential energy and its sum during a MD simulation at $k_B T/\epsilon = 0.01$ of a dimer in the presence of several unbonded particles. In the time interval reported in the figure, three swapping events are observed. As can be seen in the figure, the total potential energy is approximatively constant and equal to $-\epsilon$ even during the swap process during which the additional stabilising energy of the further bond is properly compensated by the repulsive three-body contribution.

One can also notice that the three-body potential energy is different from zero only in the short time intervals in which the swapping process takes place. In this respect, the addition of the three-body potential introduces a small perturbation on the system potential energy and it does not alter significantly the system structure and thermodynamics.

To provide further evidence of the ability of the algorithm to model bond-swapping dynamics, I introduce here a system in which the only bond-breaking and bond-forming events are mediated by a bond-swapping process. The system is composed of 400 particles of type A and 600 particles of type B interacting with a spherical two-body potential. In this example, the three-body potential favour also the single-bond condition such that each particle A can bind preferentially with only one B particle, forming at very low T (when all possible bonds are formed) 400 AB dumbbell in the presence of 200 additional free B particles. These 200 unbonded particles provide the "swapper" reservoir. Particles A and particles B bind via a short-range $n - 2n$ bonding potential [21,22],

$$V_{\text{bond}}^{\text{AB}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{2n} - \left(\frac{\sigma}{r} \right)^{n} \right], \qquad (3)$$

with $n = 100$. The large value of n ensures that the AB interaction goes to zero very rapidly. For numerical convenience $V_{\text{bond}}^{\text{AB}}$ is assumed to vanish for $r > 1.3\sigma$. The A-A and B-B interactions are purely repulsive and modelled via a generalized $n - 2n$ WCA potential

$$\begin{cases} V^{\text{AA}}(r) = V^{\text{BB}}(r) = \\ 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{2n} - \left(\frac{\sigma}{r} \right)^{n} \right] + \epsilon, & r < 2^{1/n}\sigma, \\ V^{\text{AA}}(r) = V^{\text{BB}}(r) = 0, & r > 2^{1/n}\sigma. \end{cases} \qquad (4)$$

The three-body potential acts on particles triplets formed by AB bonds (*e.g.* V_{bond} in eq. (2) coincides with $V_{\text{bond}}^{\text{AB}}$). In this simplified model the three-body potential is crucial for controlling the dimeric structure of the fluid. In the absence of the three-body potential, at low T A and B particles would associate into a large compact cluster to minimise, via formation of multiple bonds per particle, the system potential energy. In the presence of the three-body potential the system at low density is composed of well defined dumbbells (equal to the number of the minority species, A in the present example) and isolated particles (of the majority species, B here), with ratios fixed by the relative concentrations. Figure 2 shows the time dependence of the bond autocorrelation function $n_b(t)$. The function provides the fraction of bonds still alive at time t, *i.e.* the fraction of bonds which where present at time zero and which are still present after time t. Since the MD simulation is performed at low T, activated bond breaking events are extremely rare. Thus, the exponential decay of $n_b(t)$ provides clear evidence of the effectiveness of the bond-swapping mechanism. While at each time the system is always composed of the same
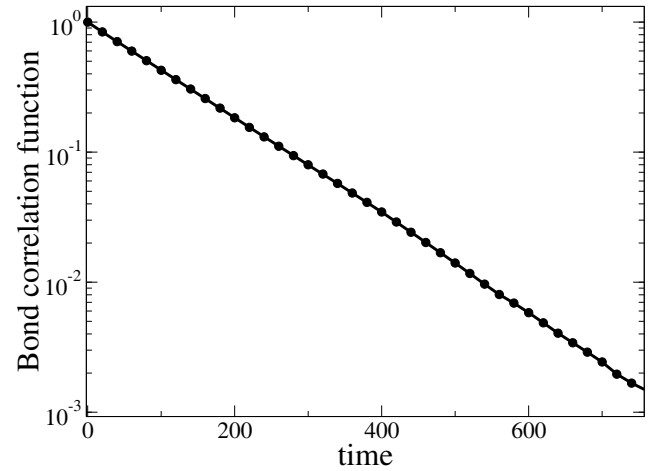

Fig. 2. Time dependence of the bond autocorrelation function for a binary mixture of AB particles interacting with the potential in eqs. (3) and (4). Here $k_B T/\epsilon = 0.03$. $n_b(t)$ decays exponentially ($n_b(t) = \exp(-t/\tau)$) with a characteristic time $\tau = 116$. Time is measured in MD units ($\sqrt{m\sigma^2/\epsilon}$).

number of dumbbells, the identity of the particles composing the dumbbells constantly changes. In the specific example here reported, $k_B T/\epsilon = 0.03$ and the total number density $\rho\sigma^3 = 0.125$. For larger values of the density, a persistent three-body contribution to the energy arises, signalling the reached limit of validity and meaningfullness of the model. I note on passing that in the cases in which bonds are defined between specific sites of larger particles (*e.g.* reactive sites along a polymer chain or patchy sites in specific position on a particle surface) the three-body interactions act only on a sub-set of the sites composing the system. In such cases density limitation may never arise, being pre-empted by crystallization or by a glass transition.

I conclude by noting that the numerical trick proposed in this paper can be exploited to investigate models of network-forming materials (including polymers) either in the case in which stochiometry controls the number of reactive particles or in the case of thermally activated network defects. The method can also be exploited (via the change in λ) to investigate the role of the bond lifetime on the decay of density fluctuations [23–25] and on the cross-over from physical to chemical bonds.

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