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Non-Markovian melting: a novel procedure to generate initial liquid like phases for small molecules for use in computer simulation studies

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Abstract

Computer simulations of liquid phases require an initial configuration from which to begin. The preparation of such an initial configuration or ‘snapshot’ often involves the melting of a solid phase. This melting is usually undertaken by heating the system at low pressure, followed by a lengthy re-compression and cooling once the melt has formed. This note looks at a novel technique to produce a liquid phase from a perfect crystal using a standard Monte Carlo simulation code.

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1. Introduction

An important prerequisite for the simulation of liquid phases is the generation of a suitable initial configuration or ‘snapshot’. Given that the density of such materials is often close to that of the crystalline solid (or even higher in the case of water) this is not a trivial task. Simply placing atoms or molecules into the sim-

ulation ‘box’ in a haphazard fashion is almost always destined to fail; there being a high probability of either overlap for ‘hard-core’ systems, or the generation of very high energy configurations for ‘soft’ potentials. The approach generally adopted to this situation is to start from a perfect crystalline structure (see [1]) and then either heat the solid to beyond its melting point or simply expand the system to a low density state (this can be done either by reduction of pressure or more simply by enlarging the simulation box) so that the solid melts. Once the system has melted (this melting process being judged perhaps by some sort of order pa-

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parameter), the system is then compressed and/or cooled to the desired thermodynamic conditions and an often substantial equilibration run performed. To complicate the situation further, it should be stated that in computer simulations the solid does not melt at the thermodynamic melting temperature (at a given constant pressure) or at the equilibrium melting pressure (at a given constant temperature). In simulation studies of bulk solid phases where no free surface is present superheating (super-expansion) of the solid phase is the rule rather than the exception [2–5]. In fact the temperature at which a solid phase melts at constant pressure is usually 20–30% higher than the equilibrium melting point. For this reason free energy calculations are used to determine the equilibrium melting point of a model T_m , where the pressure and chemical potential of both phases are identical. An alternative method is to create a solid–liquid interface and allow this to reach equilibrium [6]. Once a coexistence point is known, the rest of the melting curve can be traced out using the Gibbs–Duhem integration technique [7,8].

Algorithms do exist to produce an initial disordered system, such as the ‘Skew Start’ method implemented in the Molecular Dynamics simulation code ‘*Moldy*’ [9]. However, in this work a simple technique is presented that provides a rapid path to the production of liquid phases. This technique can be applied to many Monte Carlo [10,11] simulation codes and requires no changes to be made to the source code.

In general no computer simulation is truly ergodic, i.e. it does not have time to visit *all* of the points in phase space. However, one hopes that the duration of the simulation is such that the trajectory followed is representative of the system. After a sufficiently long run one hopes that the system is in its equilibrium state and ensemble averages yield correct (to within statistical uncertainty) values for thermodynamic quantities. Note that for complex systems a ‘sufficiently long’ run may be very long indeed. Facing the problem of ‘broken ergodicity’ has led to the development of special Monte Carlo (MC) methods, such as the Jump-Walking technique developed by Frantz et al. [12]

In any MC simulation the quality of the random number generator (RNG) used is of fundamental importance. Producing a series of pseudo-random numbers from arithmetical methods is a far from trivial task, and much effort has been devoted to this subject (see [13]). Indeed, given the exact solution for the

2-d Ising model, Monte Carlo simulations have been used as a test of the quality of random number generators [14,15], a test which many so-called ‘good’ RNG’s have failed.

In this paper we describe an interesting observation which, to the best of our knowledge, has not been previously reported. It has been found that when performing short, consecutive Monte Carlo simulations, using the final configuration of the previous run as the initial configuration of the new run, and maintaining the same initial seed throughout the consecutive Monte Carlo runs then solid phases melt even for temperatures below the melting point, T_m . The decay of the solid structure is due to the non-Markovian character of the Monte Carlo simulations when performed as described. Although the Metropolis importance sampling scheme is used to accept the trial configurations, the principle of detailed balance or microscopic reversibility is not satisfied. A number of short consecutive Monte Carlo runs is equivalent to periodically restarting the RNG from the same initial point during a simulation. This resetting of the RNG breaks the Markov chain.

Here use is made of this “non-Markovian” melting for practical purposes. By taking a disrupted configuration, and by subjecting it to a standard equilibration run, results are produced that agree very well with systems obtained via much more circuitous routes involving many more simulation cycles.

Three examples are presented, a simple Lennard-Jones system, an ionic salt (NaCl), and the melting of ice- I_h to liquid water.

1.1. Simple system: The Lennard-Jones fluid

A system of 256 atoms, interacting via the Lennard-Jones 12-6 (LJ) potential [16], were arranged in a face centered cubic close packed structure (see Fig. 1). For the Lennard-Jones system the thermodynamic state is described in terms of reduced units [17] such that $\rho^* = (N/V)\sigma^3$, $p^* = p/(\epsilon/\sigma^3)$ and $T^* = T/(\epsilon/k)$ where ϵ and σ are the parameters of the LJ potential, N is the number of molecules (or atoms in this case) of the system, and V is the total volume. For Canonical ensemble (NVT) simulations one MC cycle includes one trial move per particle (either a translational move, or for non-spherical molecules, a rotational move). For NpT simulations a trial change in the volume of the

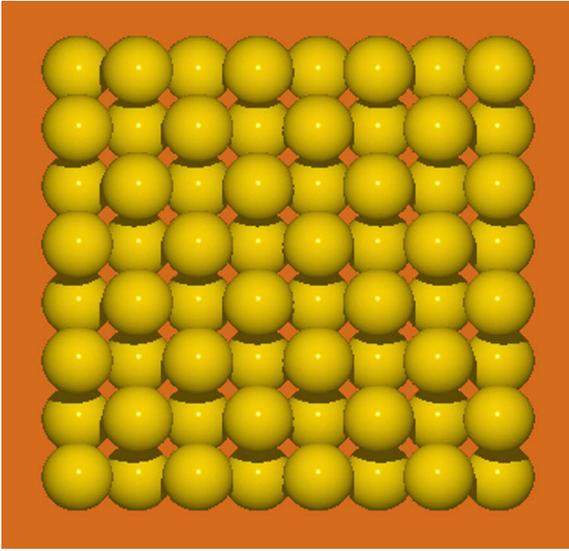


Fig. 1. Snapshot of the perfect lattice of Lennard-Jones atoms. ($I_{hkl} = 1.00$.)

system is also performed. The pair potential was truncated at $r = 2.7\sigma$, and standard long range corrections to the energy were added.

It is often useful to quantify the degree of order in a system with a suitable order parameter. In this study the intensity of the Bragg reflection from the hkl planes of the crystal structure is used:

$$I_{hkl} = |F_{hkl}|^2 = F_{hkl} F_{hkl}^* \quad (1)$$

which is given by the square of the structure factor defined as:

$$F_{hkl} = \frac{1}{N} \sum_{i=1}^{i=N} f_i \exp(2\pi i(hx_i + ky_i + lz_i)), \quad (2)$$

where x_i , y_i and z_i are coordinates of molecule i relative to the vectors that define the simulation box. The atomic scattering factor, f_i was arbitrarily set to one. For hkl the planes with the most intense line were chosen. For the perfect face centered cubic solid $I_{hkl} = 1$, and for an isotropic liquid $I_{hkl} = 0$.

The LJ solid was studied by performing NpT simulations at $T^* = 0.75$ and $p^* = 1.00$. Under these conditions the thermodynamically stable phase is the solid [18,19]. As an illustration of this stability an NpT simulation was performed. After 200 000 cycles the average value of I_{hkl} of the Monte Carlo run was $I_{hkl} = 0.72$ and the density was $\rho^* = 0.98$. A snapshot

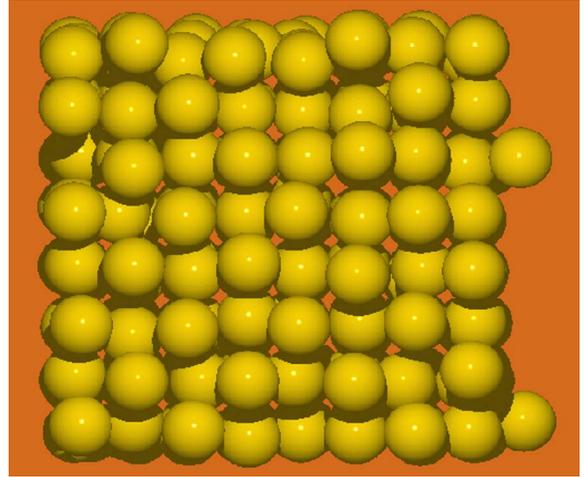


Fig. 2. Snapshot of the Lennard-Jones system after 200 000 NpT MC cycles. Results for $T^* = 0.75$, $p^* = 1.00$. The average value of the density and of the order parameter obtained from this NpT run are $\rho^* = 0.98$ and $I_{hkl} = 0.72$, respectively.

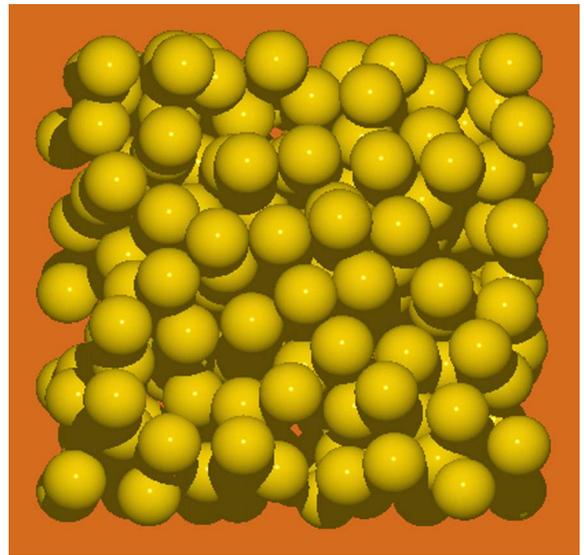


Fig. 3. Snapshot of the disordered Lennard-Jones system after only 20 runs of 10 NVT Monte Carlo cycles. The runs were performed at $T^* = 0.75$, $\rho^* = 0.98$. The order parameter of the snapshot is $I_{hkl} = 0.001$.

of this final configuration is shown in Fig. 2. In contrast to this situation, 20 consecutive runs of 10 NVT Monte Carlo cycles are performed at the same temperature, also starting from the perfect crystal structure with $\rho^* = 0.98$. Each final configuration of a Monte

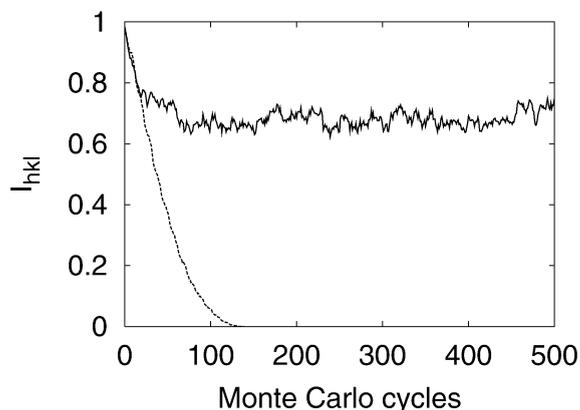


Fig. 4. Plot of the decay of I_{hkl} for the LJ system with respect to the number of Monte Carlo cycles. Dashed line for 20 runs of 10 NVT MC cycles ($T^* = 0.75$, $\rho^* = 0.98$) compared with the first 500 MC cycles of a standard NpT run (solid line) performed at $T^* = 0.75$, $\rho^* = 1.00$ (after 200 000 cycles $I_{hkl} = 0.72$).

Carlo run becomes the initial configuration for the subsequent run, whilst maintaining the same initial seed for the RNG. The result of this brief process of only 200 MC cycles is presented in Fig. 3. The evolution of I_{hkl} as a function of the number of cycles is presented in Fig. 4 for both the non-Markovian melting and a standard NpT run. The structure factor decays rapidly, having $I_{hkl} = 0.001$ after 200 MC cycles. The result is dramatically different from that of the plateau reached by the standard run; the initial crystal structure is now completely disrupted. This disrupted configuration was then equilibrated for 15×10^3 cycles in a standard NpT MC run. The density and internal energy obtained for the supercooled liquid is $\rho^* = 0.8779$ and $U/NkT = -8.3216$, which compares extremely well with $\rho^* = 0.8782$ and $U/NkT = -8.3236$ for the liquid phase obtained by melting the solid at high temperatures and then slowly cooling the system back down to $T^* = 0.75$ and $\rho^* = 1.00$.

1.2. Ionic system: Simulation of NaCl

In this section an ionic system is studied in a similar fashion to that of the Lennard-Jones described in the previous section. The system comprised of 512 ions, half sodium and half chlorine, with the $Fm\bar{3}m$ space group (Fig. 5). The parameters for this model are taken from Ref. [20]. The ions consist of a LJ potential plus a Coulombic charge, either e or $-e$, lo-

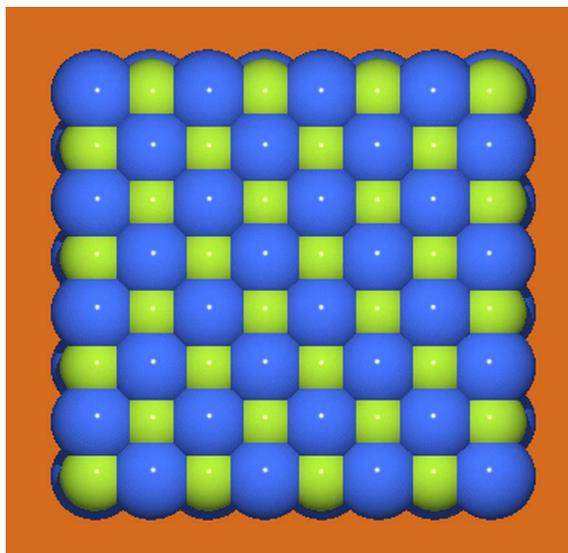


Fig. 5. Snapshot of the perfect lattice of NaCl. ($I_{hkl} = 1.00$.)

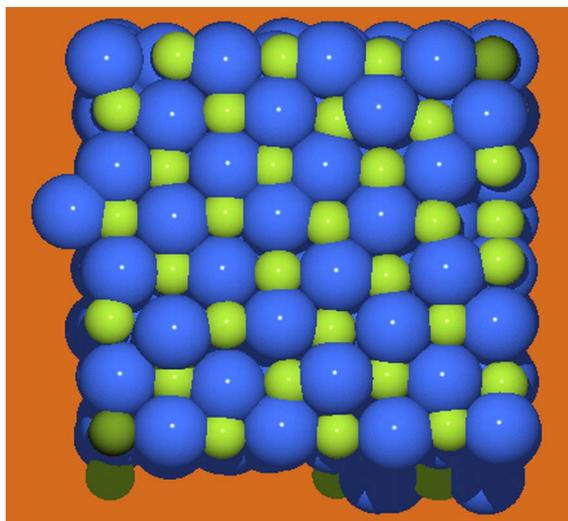


Fig. 6. Snapshot of the NaCl system after 200 000 NpT MC cycles at 1200 K and 1 bar. The average density and translational order parameter obtained from the run is $\rho = 1.7 \text{ g/cm}^3$ and $I_{hkl} = 0.748$, respectively.

located at the center of the ion. The melting point for this model was calculated to be $T_m = 1304 \text{ K}$ at $p = 1 \text{ bar}$ [21] by means of free energy calculations using the Frenkel–Ladd method for the solid phase [22]. The LJ potential is truncated at $r = 10.6 \text{ \AA}$ and long range corrections to the energy were accounted for. Electrostatics were treated using the Ewald sum technique [23].

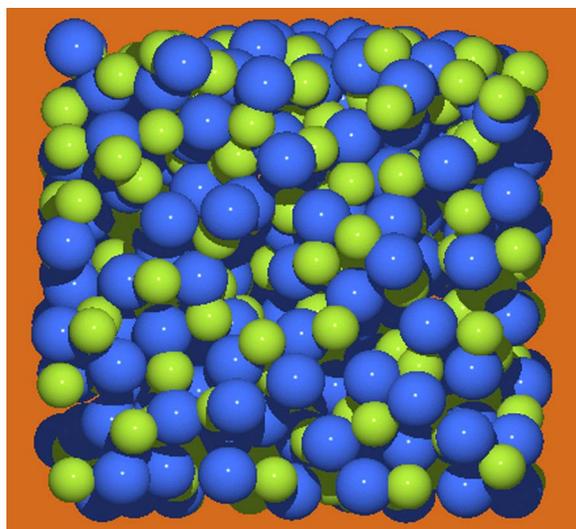


Fig. 7. Snapshot of the disordered NaCl system after only 10 runs of 10 *NVT* Monte Carlo steps at 1200 K and $\rho = 1.7 \text{ g/cm}^3$. The value of the translational order parameter of the snapshot is $I_{hkl} = 0.02$.

With this in mind non-Markovian melting was undertaken at a temperature of $T = 1200 \text{ K}$ and $p = 1 \text{ bar}$. In principle, at this temperature and pressure the solid is the stable phase, and this was indeed the case during a standard NpT MC run of 200 000 cycles (see Fig. 6). The resulting structure factor is $I_{hkl} = 0.748$ and $\rho = 1.7 \text{ g/cm}^3$ (note that $I_{hkl}^{\text{perfect}} = 1$). However, after 10 consecutive *NVT* Monte Carlo runs of 10 cycles ($T = 1200 \text{ K}$, $\rho = 1.7 \text{ g/cm}^3$), again repeating the RNG seed as in the LJ case, I_{hkl} drops to 0.02. The corresponding snapshot of this structure is shown in Fig. 7.

Once again, the disordered configuration obtained from non-Markovian melting was equilibrated in the NpT ensemble for 5×10^3 cycles, followed by a production run of 15×10^3 cycles. This resulted in a system with a density of $\rho = 1.28 \text{ g/cm}^3$ and an internal energy of $U = -171.3 \text{ kcal/mol}$. This compares very well with $\rho = 1.28 \text{ g/cm}^3$ and $U = -171.4 \text{ kcal/mol}$ obtained for a supercooled system of NaCl obtained from the standard route (i.e. heating the solid until it melts and then cooling it slowly).

In Fig. 8 the results of changing the number of MC cycles in *NVT* runs before repeating the seed is presented. These results were obtained for $T = 1200 \text{ K}$, $\rho = 1.7 \text{ g/cm}^3$. It is interesting to note that non-Markovian melting occurs for runs of up to 60 cycles.

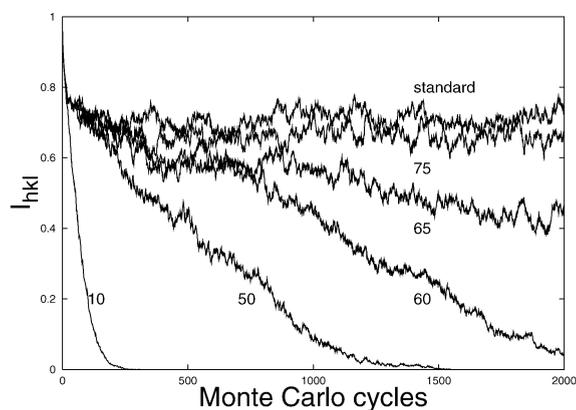


Fig. 8. Plot of I_{hkl} with respect to the number of MC cycles for contiguous block of 10, 50, 60, 65 and 75 cycles along with a standard *NVT* MC simulation for NaCl at $T = 1200 \text{ K}$ and $\rho = 1.7 \text{ g/cm}^3$.

However, for runs of 75 cycles the effect is reduced to a slight drop in I_{hkl} .

1.3. Molecular system: Simulation of supercooled water

In this example we present the case of a molecular fluid; water. To describe water the TIP4P [24] model was used. This model consists of a LJ site located on the oxygen atom, two positive charges located on the hydrogen atoms, and a negative charge is located 0.15 \AA from the oxygen along the bisector of the H–O–H angle. The LJ potential was truncated at $r = 8.5 \text{ \AA}$ and long range corrections to the energy were accounted for. Electrostatics were treated using the Ewald sum technique. The TIP4P is one of the most popular models of water used in biological simulations. The melting temperature at $p = 1 \text{ bar}$ of ice I_h for this model has been determined recently to be 232 K [25–27]. The ‘normal’ path to producing a system of super-cooled water would be to take a crystalline water structure, typically ice I_h [28], and melt it at a high temperature. For the TIP4P model a ‘high’ temperature would be one in excess of 310 K [3,4]. Once the system had melted it would then be cooled to 230 K involving a substantial period for equilibration. In this example the system simulated consists of 432 TIP4P [24,27,29] water molecules in the ice- I_h crystal structure.

As before, two simulations were performed. In the first simulation a standard MC run of 200 000 cycles

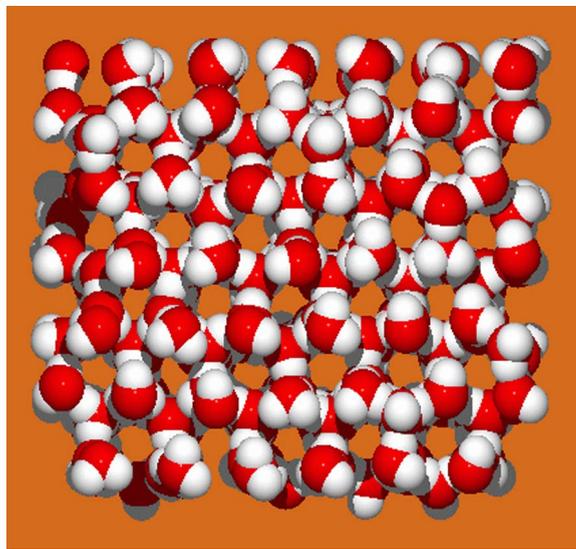


Fig. 9. Snapshot of ice- I_h after 200 000 NpT Monte Carlo steps at 230 K and 1 bar. The hexagonal lattice is still evident. The average value of the density and of the translational order parameter obtained in the run is $\rho = 0.94 \text{ g/cm}^3$ and $I_{hkl} = 0.284$, respectively.

was undertaken in the NpT ensemble at a temperature of $T = 230 \text{ K}$ and $p = 1 \text{ bar}$, yielding a density of $\rho = 0.94 \text{ g/cm}^3$. At this temperature and pressure the solid is the thermodynamically stable phase. From this final configuration, 20 consecutive runs of 10 NVT Monte Carlo cycles each (i.e. 200 cycles in total) are performed, and as before, each simulation was initiated from the output configuration of the previous run, whilst maintaining the RNG seed the same in each case.

In Fig. 9 we see the result of a single run of 200 000 Monte Carlo cycles and in Fig. 10 we see the result of 20 runs of 10 Monte Carlo cycles. In the case of the 200 000 cycles simulation we see that the crystal lattice has remained largely unchanged apart from small displacements about the mean positions of the molecules with ($I_{hkl} = 0.284$). This is what one should expect since we are simulating below the melting temperature of the model. However, in contrast we can see that after only 20 runs of 10 Monte Carlo cycles the crystal structure is all but lost. This structureless system was then simulated for 1.2×10^5 conventional NpT MC cycles. This resulted in a system with a density of $\rho = 0.99 \text{ g/cm}^3$ and an internal energy of -11.01 kcal/mol . This compares very well with a density of $\rho = 1.00 \text{ g/cm}^3$ and an internal energy

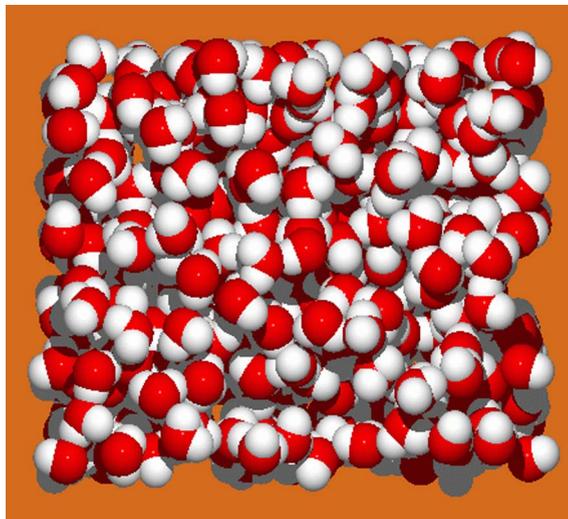


Fig. 10. Snapshot of the ice- I_h system after 20 runs of 10 NVT Monte Carlo steps at 230 K and $\rho = 0.94 \text{ g/cm}^3$. The translational order parameter of the final snapshot is $I_{hkl} = 0.002$.

of -10.98 kcal/mol obtained via a standard heating–melting–cooling simulation route.

2. Conclusion

By using a short period RNG (i.e. a number of consecutive, very short simulations maintaining the same initial RNG seed) it is possible to rapidly disrupt the crystal structure, even below the melting temperature of the model under consideration. This phenomena is a result of the non-Markovian character of the simulations. Once this disordered configuration has been obtained (typically within 100–200 cycles, less than 1 min of CPU on a standard personal computer) it is then possible to perform a standard simulation Monte Carlo to obtain an equilibrated supercooled liquid. In the examples in this work a ‘short’ period is between $\approx 15\,000$ and $\approx 30\,000$ random numbers, i.e. 10 cycles of 6 random numbers (particle choice, choice of move, 3 displacements which can be either of translational or of rotational type and acceptance) for 250–500 molecules.

The methodology has been tested for three different systems, the simple Lennard-Jones system, the ionic NaCl model and the TIP4P model of water. Advantages of this method for liquids is that it is not nec-

essary to raise the temperature of the system, thus avoiding the creation of high energy molecular conformations. Another feature is that it is independent of the RNG and it is not necessary to modify the source of the simulation code, which may not always be available.

It is worth noting that once a disordered state has been formed it is very rare to observe re-crystallization in simulation studies, this requiring the activated process of nucleation. As an example of this the re-crystallization of water to ice I_h has only ever been seen once during a computer simulation [30].

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