A finite-temperature Monte Carlo algorithm for network forming materials

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Computer simulations of structure formation in network forming materials (such as amorphous semiconductors, glasses, or fluids containing hydrogen bonds) are challenging. The problem is that large structural changes in the network topology are rare events, making it very difficult to equilibrate these systems. To overcome this problem, Wooten, Winer and Weaire [Phys. Rev. Lett. 54, 1392 (1985)] proposed a Monte Carlo bond-switch move, constructed to alter the network topology at every step. The resulting algorithm is well suited to study networks at zero temperature. However, since thermal fluctuations are ignored, it cannot be used to probe the phase behavior at finite temperature. In this paper, a modification of the original bond-switch move is proposed, in which detailed balance and ergodicity are both obeyed, thereby facilitating a correct sampling of the Boltzmann distribution for these systems at any finite temperature. The merits of the modified algorithm are demonstrated in a detailed investigation of the melting transition in a two-dimensional 3-fold coordinated network.

I. INTRODUCTION

Network forming materials are ubiquitous in nature, common examples being semiconductors such as silicon and silica, as well as fluids that can form hydrogen bonds. What these materials have in common is that their topology on short length scales is governed by certain rules. For example, in amorphous silicon, most atoms are 4-fold coordinated, the preferred Si-Si bond length being \( \approx 2.35 \) Å, and the preferred Si-Si-Si bond angle being the tetrahedral angle. This complicates molecular dynamics simulations of these materials, where the particles spend most of their time thermally fluctuating about their equilibrium positions, while large structural changes in the network topology are rare. This is particularly cumbersome if well-relaxed amorphous networks are needed, i.e. networks that locally fulfill the bond requirements (and thus have a low energy) but where long-ranged order is absent.

To overcome this problem, Wooten, Winer, and Weaire (WWW) proposed a Monte Carlo algorithm using a bond-switch move \[1\]. This move can be applied to any system whose potential energy \( E \) is defined via a connectivity table, i.e. an explicit list specifying which particles are connected to each other by bonds (the prototype example of such a potential is the Keating potential \[2\], see also Eq. \([2]\)). The bond-switch move proceeds as shown in Fig. 1. First, a cluster \( \{A, B, C, D\} \) of four particles is selected randomly, containing the bonds \( \{AB, AC, BD\} \) with the constraint that \( A \) may not be bonded to \( D \), nor \( B \) to \( C \). Next, a change in the network topology is proposed, whereby the bonds \( AC \) and \( BD \) are removed from the connectivity table, and replaced by two new bonds, \( AD \) and \( BC \). The change is accepted with the Metropolis probability

\[
P_{\text{acc}} = \min[1, e^{-(E'_F-E'_I)/k_BT}],
\]

with \( E'_F \) (\( E'_I \)) the energy before (after) the bond-switch, \( T \) the temperature, and \( k_B \) the Boltzmann constant. The prime (') indicates, and this point is crucial, that the energy is to be measured with all the particles in the network placed at their equilibrium positions. That is, for a given network topology (connectivity table) the particle positions are fixed deterministically by energy minimization.

The WWW algorithm is thus primarily aimed at modifying the network topology, while thermal fluctuations of the particles about their equilibrium positions are ignored (note the contrast with molecular dynamics). Unfortunately, it does so at a cost: By deterministically fixing the particle positions at every move ergodicity is broken. Hence, the WWW algorithm does not sample the Boltzmann distribution at finite \( T \). In its original formulation \[1\] this issue was irrelevant, since there the goal was simply to generate a well-relaxed (low energy) amorphous network (the algorithm thus being merely an optimization tool). However, if one wishes to study temperature-driven phase transitions in these systems, then the original WWW algorithm needs to be modified. The aim of this paper is to present such a modification, and to use it to study the melting transition of a two-dimensional 3-fold coordinated network.
II. MODEL

To be specific, we consider a two-dimensional $A = L_x \times L_y$ system with periodic boundaries containing $i = 1, \ldots, N$ particles. To each particle $i$, a vector $\vec{r}_i = (x_i, y_i)$ is assigned to denote its position in the plane, as well as three integers $\{j, k, l\}$ which denote the labels of the three particles to which particle $i$ is bonded. The energy is given by the Keating potential \[ E = \frac{3\alpha}{16d^2} \sum_{\{ij\}} (\vec{r}_{ij} \cdot \vec{r}_{ij} - d^2)^2 + \frac{3\gamma}{8d^2} \sum_{\{ijk\}} (\vec{r}_{ij} \cdot \vec{r}_{ik} + \frac{1}{2}d^2)^2, \] with $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$, and parameters $d = 2.35$ Å, $\alpha = 2.965$ eV Å$^{-2}$, $\gamma = 0.285\alpha$ (which are the parameters for bulk silicon). The first term is a two-body interaction which equates the preferred $i-j$ bond length to $d$; the second term is a three-body interaction which sets the preferred $j-i-k$ bond angle to 120 degrees (as appropriate for a two-dimensional system). The sums in Eq. (2) extend over bonded particles in the connectivity table only. For a system containing $N$ particles, there are $3N/2$ two-body terms, and $3N$ three-body terms. The computational effort of the energy calculation thus scales linearly with $N$.

Note on units and conventions

In what follows, the $NVT$-ensemble is used at density $\rho = N/A = 8/(6\sqrt{3}d^2)$, box aspect ratio $L_x/L_y = 3/(2\sqrt{3})$, and $N = 8n^2$, with $n$ an integer. In this way, the box always “fits” the groundstate of Eq. (2), i.e. a perfect honeycomb lattice with lattice constant $d$ (the corresponding energy thus being $0$). All reported temperatures are given in units of eV/$k_B$, while free energies (and free energy differences) are reported in units of $k_B T$.

III. THE MODIFIED BOND-SWITCH MOVE

Consider now a network configuration (i.e. a set of particle positions and a connectivity table) in which a cluster of four particles $c \in \{A, B, C, D\}$ has been selected according to the WWW bond-switch move of Fig. 1. Let $\vec{I}_c$ denote the initial positions of these four particles. Next, perform a local energy minimization, whereby only the positions of the four particles in the cluster are allowed to change, keeping the positions of all the other particles in the network, as well as the connectivity table, fixed. The resulting positions are denoted $\vec{P}_c$. The modification of the WWW algorithm is based on the observation that, irrespective of the initial positions $\vec{I}_c$, the positions $\vec{P}_c$ obtained after local energy minimization are always the same.

This property can be exploited to modify the bond-switch such that both detailed balance and ergodicity are obeyed: The cluster $c$ is selected as before; the initial positions $\vec{I}_c$, and the positions $\vec{P}_c$ obtained after local energy minimization, are recorded. Next, one performs the bond-switch, immediately followed by a second local energy minimization where, as before, only the particles in the cluster are allowed to move; the resulting positions $\vec{Q}_c$ are recorded. Finally, a stochastic process is used to generate four random displacements $\vec{\Delta}_c$ around $\vec{Q}_c$, which yield the final positions of the four particles: $\vec{Q}_c + \vec{\Delta}_c$. The resulting network configuration is accepted with probability \[ P_{acc} = \min \left[ 1, \frac{\Pi(W(\vec{I}_c - \vec{P}_c)) e^{-\left(E_P-E_I\right)/k_B T}}{\Pi(W(\vec{\Delta}_c))} \right], \] which ensures that detailed balance is maintained. Here, $W(\vec{r})$ is the probability that the stochastic process (still to be specified) selects the vector $\vec{r}$. Note that, in contrast to Eq. (1), the energies $E_P$ and $E_I$ refer to the actual network energy (and not the energy obtained after minimization with respect to the particle positions).

Provided the selection process used to generate the displacements $\vec{\Delta}_c \equiv (\Delta X_c, \Delta Y_c)$ is ergodic, this algorithm faithfully samples the Boltzmann distribution at temperature $T$. Its efficiency is set by the details of the selection process. With the particles placed at their locally minimized positions $\vec{Q}_c \equiv (X_c, Y_c)$ the energy can be approximated as \[ E \approx \frac{1}{2} \sum_c \Delta_{c, H} \cdot \vec{H}_c \cdot \vec{\Delta}_c, \] where $E_{\alpha\beta}$ is the second derivative of $E$ with respect to $\alpha$ and $\beta$ (to be evaluated at the minimized positions). Since Eq. (4) is quadratic in the displacements, the latter are Gaussian distributed in thermal equilibrium. A good choice is therefore to draw $\Delta X_c$ from the Gaussian probability distribution \[ W(\Delta X_c) = \frac{1}{\sqrt{2\pi}\sigma_{X,c}} \exp(-\Delta X_c^2/2\sigma_{X,c}^2), \] with $\sigma_{X,c}^2 = k_B T E_{Y,Y_c}/\det \vec{H}_c$, and similarly for $\Delta Y_c$ where $\sigma_{Y,c}^2 = k_B T E_{X,X_c}/\det \vec{H}_c$. Note that, by drawing from a Gaussian distribution, every displacement has a finite probability of being selected, and so ergodicity is trivially fulfilled. Since the components of $\vec{\Delta}_c$ are selected independently, it holds that $W(\vec{\Delta}_c) \propto W(\Delta X_c) \times W(\Delta Y_c)$. The computation of the reverse weight $W(\vec{I}_c - \vec{P}_c)$ proceeds analogously, but with the derivatives evaluated at $\vec{P}_c$ before the bonds were switched.

The algorithm just described samples the network topology and the particle positions simultaneously, which
suffices for a simulation. Still, to facilitate faster equilibration, it helps to also use a move whereby only the particle positions are updated. To this end, one can use the same scheme as above, but not switch the bonds, such that $\tilde{P}_c = \bar{Q}_c$ (and so only one local energy minimization is required). For this displacement move, it suffices to select just a single particle (as opposed to a cluster of four). In the results to be presented, both single-particle displacement and WWW moves were used, each attempted with equal a priori probability [4].

As a first test, we plot in Fig. 2 how the specific heat per particle $C_V$ with the temperature $T$ as obtained using our algorithm for a network containing $N = 128$ particles. Simulations were performed at $T = 0.35, 0.40, 0.45, 0.50$ (indicated by the dots) with the results of each run subsequently extrapolated over a range $\Delta T = \pm 0.05$ using the single histogram method [5, 6].

IV. RESULTS: MELTING OF A 2D NETWORK

The melting transition in the Keating model Eq. (2) is from a low-temperature ordered phase, to a high-temperature disordered phase. At zero temperature, the particles form a perfectly ordered honeycomb lattice, while at high temperature the network is spatially disordered (particle positions random beyond a certain finite range). Consequently, a phase transition must occur, at some finite transition temperature $T_c$. The aim of this section is to determine $T_c$, as well as to characterize the transition type (expected to be first-order). To this end, we use the hexatic bond-order parameter [8]

$$q_6 = \frac{2}{3N} \sum_{\{ij\}} \exp(i6\theta_{ij})$$

with the sum over all bonds in the connectivity table (i.e. a total of $3N/2$ terms), and where $\theta_{ij}$ is the angle of the bond between particles $i - j$ with respect to an arbitrary reference axes (say, the $x$-axes). In the perfectly ordered phase (honeycomb lattice) $q_6 = 1$, while for the disordered phase $\lim_{N \to \infty} q_6 = 0$ (since Eq. (6) uses the absolute value, $q_6$ is never exactly zero, but it approaches this value in a disordered system as the system size is increased).

A. Analysis of the free energy

We will analyze the melting transition via the corresponding order parameter distribution $P(q_6)$, defined as the probability to observe a network with order parameter $q_6$. The physical significance of $P(q_6)$ is its relation to the free energy, $F(q_6) = -k_B T \ln P(q_6)$, providing a convenient means to study the phase behavior. To ensure that $P(q_6)$ gets accurately measured, we combine our Monte Carlo scheme with a number of high-resolution tools commonly used in the study of phase transitions (see Appendix).

In Fig. 3(a), we show typical free energy curves obtained at three different temperatures. At the highest considered temperature, $F(q_6)$ reveals a global minimum at a low value of $q_6$, meaning that the disordered phase is the thermodynamic stable one (solid curve). A typical snapshot of the disordered phase is shown in Fig. 3(b), which reveals a structure containing mostly 6-fold rings, but with many defects (i.e. rings that are smaller or larger). At low temperature, $F(q_6)$ attains its minimum at a significantly larger value of the order parameter (dotted curve). This means that the ordered phase has become the stable one. The corresponding snapshot is shown in Fig. 3(c), which reveals a rather ordered structure (however, defects do remain; see Section IV D). By tuning the temperature to a special value, $T = T_H$, the two minima in the free energy occur at the same height (dashed curve), which marks the phase transition. Note that the free energy curves in Fig. 3(a) are characteristic of a first-order phase transition, as the global minimum jumps discontinuously from $q_{6\text{dis}}$ to $q_{6\text{ord}}$ as $T$ is lowered.

B. Finite-size scaling analysis

The temperature $T_H$ where the free energy minima are at equal height depends on the size of the system $T_H \equiv$
In the thermodynamic limit, the disordered (b) and ordered (c) phase (vertices represent particle positions; edges represent bonds). All results in this figure refer to actual simulation data obtained using the modified bond-switch Monte Carlo move of this work.

Since it is numerically more accurate, this analysis was performed at the temperature \( T_H(N) \) of the susceptibility maximum. The positions were obtained using an integral measure

\[ q_{\text{dis}} = 2 \int_0^c q_6 P(q_6) dq_6, \quad q_{\text{ord}} = 2 \int_0^1 q_6 P(q_6) dq_6, \tag{7} \]

with the “cut-off” between the phases taken at the average of the full distribution \( c = \langle q_6 \rangle \). Fig. 4(d) shows that \( q_{\text{dis}} \) decreases with \( N \), as expected for a disordered phase, while \( q_{\text{ord}} \) saturates at a finite value, consistent with an ordered phase. Note that \( q_{\text{ord}} \sim 0.7 \) at the transition, i.e. distinctly below the value unity of the perfect hexagonal lattice. This means that the ordered phase still contains a substantial number of defects (see Section IV D).

All in all, the finite-size scaling results of Fig. 4 rather strongly indicate that the melting transition in the Keating model is first-order, as might have been expected.

**C. Phase coexistence**

The barrier \( \Delta F \) of Fig. 3(a) also has an interesting physical interpretation, which we still explore. In order to traverse from one phase to the other, a coexistence region must be crossed where both phases appear simultaneously. This region will contain a lot of interface, which is the origin of the free energy barrier (and thus explains the scaling \( \Delta F \propto \sqrt{N} \) in two dimensions). The coexistence can be directly visualized if one performs a simulation whereby \( q_6 \) is constrained to a value that is close to the maximum of the free energy curve (in practice, one performs such a simulation by rejecting those Monte Carlo moves for which \( q_6 \) strays away too much from the desired value). In Fig. 5 we show a typical snapshot obtained via this procedure. As in Fig. 3 the edges represent bonds between particles. In addition, those vertices \( i \) for which the local order parameter \( q_i \) exceeds a certain threshold (and which thus belong to the ordered phase) have been marked with a (blue) dot. As the figure strikingly shows, virtually all particles that belong to the ordered phase have condensed into one large cluster. Since the overall order parameter \( q_6 \) of the system was chosen to be around the maximum of the free energy, this cluster occupies roughly half the system area (lever-rule of phase coexistence). In addition, note that energy measured at \( T = T_H \), i.e. the temperature where the minima are at equal height. As shown in Fig. 3(a), the minima are then separated by a free energy barrier \( \Delta F \), indicated by the vertical double-arrow. At a first order transition, this barrier should scale \( \propto L^{d-1} \propto \sqrt{N} \), where \( L \) denotes the linear extension of the system, and \( d = 2 \) the spatial dimension [10, 11]. The variation of \( \Delta F/\sqrt{N} \) with \( 1/N \) is shown in Fig. 3(c), which thus should be constant; the latter holds to within an uncertainty of \( \sim 10\% \).

FIG. 3: (a) Typical free energy curves \( F(q_6) \) obtained at three different temperatures for the Keating model of Eq. (2) using \( N = 392 \) particles. The shape variations of \( F(q_6) \) are characteristic of a first-order phase transition. At \( T = T_H \), two-phase coexistence is observed, whereby \( F(q_6) \) reveals two minima of equal height. The free energy barrier then separating the phases is indicated as \( \Delta F \). The positions of the minima, marked as \( q_{\text{dis}} \) and \( q_{\text{ord}} \), reflect the value of the order parameter \( q_6 \) in the disordered and ordered phase, respectively. The snapshots show network configurations typical of the disordered (b) and ordered (c) phase (vertices represent particle positions; edges represent bonds). All results in this figure refer to actual simulation data obtained using the modified bond-switch Monte Carlo move of this work.

To accurately locate the transition temperature in the thermodynamic limit, \( T_c = \lim_{N \to \infty} T_H(N) \), requires a finite-size scaling analysis. At a first-order phase transition, one expects a shift \( T_c - T_H(N) \propto 1/N \) [2]. In Fig. 4(a), we have plotted \( T_H(N) \) versus \( 1/N \) (triangles), which can indeed be fitted quite well with a straight line (the intercept of this line yields \( T_c \)). In addition to \( T_H(N) \), it is also common to study the finite-size dependence of \( T_c(N) \), defined as the temperature where the susceptibility per particle, \( \chi = \langle q_6^2 \rangle - \langle q_6 \rangle^2 \rangle / N \), reaches its maximum (thermal averages are trivially computed from the normalized order parameter distribution \( \langle q_6^p \rangle = \int_0^1 q_6^p P(q_6) dq_6 \) ). The dots in Fig. 4(a) show the shift of the latter temperature, which also fits quite well to a straight line; combining both estimates, we obtain \( T_c = 0.323 \pm 0.003 \). Also of interest is the value of the susceptibility \( \chi_{\text{max}} \) measured at \( T_c(N) \). At a first-order transition, the latter scales \( \propto N \) [2], which we confirm in Fig. 4(b).

Next, we consider the size dependence of the free energy

\[ H = \frac{1}{2} q_6 \sum_i \sum_{j \neq i} \delta \eta_{ij} \left( \sum_k \eta_{kj} \right) \]

with the free energy functional

\[ F[q_6] = \frac{1}{2} \sum_{i,j} \delta \eta_{ij} \left( \sum_k \eta_{kj} \right) q_6 \]
FIG. 4: Finite-size scaling analysis of the melting transition in the Keating model of Eq. (2) using system sizes \(N = 72, 128, 200, 288, 392, 512, 648, 800\). (a) Variation of the pseudo-transition temperatures \(T_H(N)\) and \(T_x(N)\) with \(1/N\); the lines are linear fits, whose intercepts yield \(T_c\) of the thermodynamic limit. (b) The susceptibility maximum versus \(N\). As expected for a first-order transition, a linear increase is revealed. (c) The (scaled) free energy barrier \(\Delta F/\sqrt{N}\) versus \(1/N\); the latter is roughly constant (note the fine vertical scale). (d) The locations of the free energy minima, \(q_{\text{dis}}\) and \(q_{\text{ord}}\), obtained at \(T = T_x(N)\), versus the system size \(N\). As expected, \(q_{\text{dis}}\) of the disordered phase decays with \(N\), while \(q_{\text{ord}}\) saturates at a finite value. Note that the data for \(q_{\text{dis}}\) use an enhanced scale.

FIG. 5: Keating network obtained in a simulation where the overall order parameter was constrained to a small interval around \(q_6 = 0.4\), which is close to the free energy maximum. As temperature, we used \(T_x(N) = 0.3257\) of the susceptibility maximum, with \(N = 5000\). The snapshot strikingly reveals the two-phase coexistence that is characteristic of first-order phase transitions. As before, edges represent bonds; vertices \(i\) whose local order parameter \(q_{6,i} > 0.6\) have been marked with a (blue) dot (for each particle \(i\), \(q_{6,i}\) was computed as in Eq. (3), but with the sum restricted to particles less than five “steps” away from \(i\) in the connectivity table).

FIG. 6: Keating network obtained in an \(NVT\)-simulation at \(T = 0.3\), which is well below the transition temperature. An ordered network with a finite concentration of defect regions (red dots) is observed. The number of particles \(N = 5000\).

the cluster has arranged into a “slab” parallel to one of the edges of the simulation cell, as this shape minimizes the length of the interface contour.

D. The structure of the ordered phase

As announced, we still consider the structure of the ordered phase, i.e. the prevailing phase at low temperature. To this end, we perform an \(NVT\)-simulation at \(T = 0.3\), which is well below the transition temperature (in this simulation, the order parameter was allowed to fluctuate freely). After equilibration, we observe that the order parameter saturates at \(q_6 \approx 0.735\). In Fig. 6 we show a typical snapshot. In this case, the vertices whose local order parameter \(q_{6,i} < 0.6\) have been marked with a (red) dot, which thus correspond to disordered regions (edges, as before, represent bonds). We observe an overall ordered structure of hexagons, containing “bubbles” of regions that are disordered. In contrast to the snapshot of Fig. 5 however, these bubbles do not coalesce. Hence, the ordered phase is to be regarded as an ordered array of hexagons, but with a finite concentration of defect regions. The latter reflect thermal fluctuations, that appear at random locations in the network. As the temperature is lowered further, these defects are gradually frozen out, until, at \(T = 0\), the perfect honeycomb l-
V. DISCUSSION

In summary, we have proposed an extension of the bond-switch Monte Carlo move of Wooten, Winer, and Weaire [1], in order to correctly simulate network forming materials at finite temperature. The algorithm can be applied to systems whose potential energy is defined via a connectivity table, such as the Keating potential [2] (used in this work), or the Tu-Tersoff potential for silica [12]. A second requirement is that, for a given connectivity table, a local energy minimization performed on a small cluster of particles always yields the same positions for these particles. When these conditions are met, network configurations that faithfully sample the Boltzmann distribution are readily generated. This paves the way toward the first high-resolution simulations of these materials, since all the tools developed for the numerical study of phase transitions (finite-size scaling, transition matrix sampling, biased sampling, histogram reweighing, and so forth) can now be applied. We have illustrated the merit of this approach by performing a detailed analysis of the melting transition in a two-dimensional 3-fold coordinated Keating network, which was shown to be first-order.

As a future application, an investigation of a silica network, which is a glass former, seems particularly fruitful. There are indications [13] that the dominant mechanism in structural relaxation in these materials is, in fact, the bond-switch move of Fig. 1. In a molecular dynamics simulation, where the natural time scale is phonon-based, such bond-switches are rare events. In the present algorithm, the natural time scale is event-based, and so it should be easier to probe the long-time relaxation regime. We note that Ref. [13] also identified two other relaxation mechanisms, in addition to the bond-switch move of Fig. 1. Whether these can also be exploited as finite-temperature Monte Carlo moves remains to be investigated.

Acknowledgments

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[4] The algorithm is completely local (execution time per move independent of \(N\)). Fast convergence of the local energy minimization is obtained by updating the particle positions as \(r_{c,n+1} = r_{c,n} + \gamma H^{-1} f_{c,n}\), with “fudge factor” \(0 < \gamma \leq 1\), \(r_{c,n}\) the position of particle \(c\) at the \(n\)-th minimization step, and \(f_{c,n}\) the corresponding force acting on the particle (i.e. the negative gradient of \(E\)). Due to the simplicity of the Keating potential, derivatives can be calculated analytically. In cases where the fast minimization scheme did not converge, a safer (but slower) steepest descent method was used.
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[7] Around \(T_c\), the accept rate of the (single particle) displacement moves \(\sim 95\%\), while that of the bond-switch moves \(\sim 0.02\%\) (i.e. significantly lower). Since the algorithm is local the computational effort per move is small. Our implementation (currently a single processor version) running on an Intel Xeon E5-2660 at 2.2 GHz reaches \(\sim 1.3\) million attempted moves per minute.
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Appendix A: Transition matrix sampling

The aim of transition matrix sampling it to obtain free energy differences based on move proposal statistics,
rather than on statistics of visited states [14]. For each attempted Monte Carlo move, two matrix elements are updated [15]

\[
M(q_1, q_F) \leftarrow M(q_1, q_F) + P_{acc},
M(q_1, q_I) \leftarrow M(q_1, q_I) + 1 - P_{acc},
\]

(A1)

with \(P_{acc}\) the accept probability of Eq. (3), \(q_I\) the value of the order parameter \(q_0\) at the start of the move, and \(q_F\) that of the proposed state (since \(q_0\) is continuous, we choose a bin size \(\sim 1/N\)). The update is performed at every attempted move, irrespective of whether it is accepted. Hence, even if the accept rate is low, one still collects statistics on \(M\), which is one advantage of the transition matrix method. In cases where the initial and proposed order parameter belong to the same bin, Eq. (A1) reduces to \(M(q_1, q_I) \leftarrow M(q_1, q_I) + 1\).

The matrix elements \(M\) are used to estimate the transition probability

\[
T(q_0, q_6) = \frac{M(q_6, q_0)}{\sum_x M(q_0, x)},
\]

(A2)

which is the probability that, being in a state with order parameter \(q_6\), a state with order parameter \(q_0\) is proposed. The latter is related to the free energy

\[
F(q_6) - F(q_0) = k_B T \log \left( \frac{T(q_6, q_0)}{T(q_0, q_6)} \right) \equiv \Delta(q_0, q_6).
\]

(A3)

Hence, during the simulation, a large set of free energy differences \(\Delta(q_0, q_6)\) is collected. The best estimate of the free energy \(\bar{F}(q_6)\) is the one which minimizes the variance

\[
\sum_{\Delta} w(q_6, q_0) \left( \bar{F}(q_6) - \bar{F}(q_0) - \Delta(q_0, q_6) \right)^2,
\]

(A4)

where the sum is over all measured free energy differences. The purpose of \(w(q_6, q_0)\) is to “weigh” each measurement \(\Delta(q_0, q_6)\) according to the magnitude of the corresponding matrix elements \(M\) (we choose those weights as described in Ref. [16]). In minimizing Eq. (A4), one value of \(\bar{F}(q_6)\) is fixed; the remaining values are obtained by matrix inversion.

Appendix B: Biased sampling

To further improve the accuracy of our data, the simulations of the largest systems \((N \geq 392)\) were performed by adding a bias function \(W(q_0)\) (i.e. a function of the order parameter \(q_0\)) to the Keating energy of Eq. (2). The bias function is chosen such that the simulation visits each value of the order parameter with equal probability. That is, in the biased simulations, the goal is to observe an order parameter distribution \(P(q_0)\) that is flat (uniform sampling). In this way, the statistical quality of the data is independent of \(q_0\) (this property is particularly desirable at first-order transitions where otherwise values of \(q_0\) corresponding to phase coexistence are hardly sampled).

In the biased simulations, the accept probability of the Monte Carlo moves, Eq. (3), is replaced by

\[
P_{acc}^{bias} = \min \left[ 1, \frac{\Pi_t W(\vec{I}_t - \vec{P}_t)}{\Pi_t W(\Delta_e^t)} e^{-\frac{E_F - E_t}{k_B T} + W(q_I) - W(q_F)} \right],
\]

with \(q_I(q_F)\) the order parameter at the start (end) of the move. To obtain uniform sampling, one chooses \(W(q_0) = -F(q_0)/k_B T\), where \(F(q_0)\) is the free energy (which is \textit{a priori} unknown). In this work, we first performed a non-biased simulation until a sufficiently large range in \(q_0\) was sampled; the resulting transition matrix data was then used to compute the free energy. The biased simulations were subsequently performed using the latter free energy as bias function. Note that, in the biased simulations, the transition matrix elements are collected exactly as described in Appendix A, i.e. using the non-biased form of the accept probability, Eq. (3). In this way, the transition matrix elements \(M\) of different runs may simply be added (even if the runs themselves used different bias functions).

Appendix C: Extrapolations in temperature

Finally, we explain how the order parameter distribution \(P_0(q_0)\), measured at temperature \(T_0\), is extrapolated to obtain \(P_1(q_0)\) at a (nearby) temperature \(T_1\). To this end, we Taylor expand to second order

\[
\ln P_1(q_0) \approx \ln P_0(q_0) + \Delta \beta \frac{d \ln P_0(q_0)}{d \beta} \bigg|_{\beta = \beta_0} + \frac{1}{2} (\Delta \beta)^2 \frac{d^2 \ln P_0(q_0)}{d \beta^2} \bigg|_{\beta = \beta_0},
\]

(C1)

where \(\beta_0 = 1/k_B T_0\), and \(\Delta \beta = 1/k_B T_1 - \beta_0\). Next, we note that \(P_0(q_0) = \mathcal{T} \exp(-E/k_B T_0)\), where the trace is over all network configurations whose order parameter equals \(q_0\), and where \(E\) denotes the Keating energy. Hence, the first derivative in Eq. (C1) is simply \(-\langle E \rangle(q_0)\), i.e. the negative average value of the Keating energy in the bin corresponding to order parameter \(q_0\), while the second derivative is the energy variance \(\langle E^2 \rangle(q_0) - \langle E \rangle^2(q_0)\) in that bin (both to be measured at \(T = T_0\)). The latter quantities are readily collected in our Monte Carlo simulations: At the end of each move, one simply identifies the current order parameter bin, and updates the corresponding energy moments. Note that Eq. (C1) provides a convenient way to perform extrapolations in temperature, without having to store the full energy distribution (only the leading two moments are needed).