Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

1 Convergence Problems of the WP model

To illustrate the convergence problem of the WP model, we reproduce the simulation in a work of O. Kahn's[1] using the WP model with various sweeping rates. For the WP model, we employ the canonical (N, V, T)-ensemble and consider a simple square lattice of $N = n^2$ sites with periodic boundary conditions. At each step in a MC simulation, we randomly choose one site, say i, flip its spin s_i to $-s_i$, and then accept or reject the new state according to the Metropolis probability

$$P(s_i \to -s_i) = \min[1, \exp(-\Delta\mathcal{H}/k_\mathrm{B}T)],$$

where $\Delta\mathcal{H}$, according to eqn (4) in the paper, is

$$\Delta\mathcal{H} = -h^{\mathrm{WP}}(T)s_i + J^{\mathrm{WP}} s_i \sum_{\langle j \rangle} s_j.$$

Since larger simulation cells usually requires longer MC simulation time, we use the Monte-Carlo step (MCS) to measure the total number of simulation steps. One MCS is equal to N-simulation steps such that in one MCS all sites in the simulation cell are checked once on average.[?] In this simulation, a 500×500 2D square lattice is considered, with $\varDelta = 1440\,\mathrm{K}$, $g = 1331$ (correspondingly, $\Delta H = 12\,\mathrm{kJ \cdot mol^{-1}}$ and $\Delta S = 60\,\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, or in Kahn's original form $\Delta H = 1000\,\mathrm{cm^{-1}}$ and $\Delta S = 5\,\mathrm{cm^{-1} \cdot K^{-1}}$), $T_{1/2} = 200\,\mathrm{K}$, $J_{\mathrm{thresh}} = 88.2\,\mathrm{K}$. Kahn took $J = 107.9\,\mathrm{K}$ (i.e. $75\,\mathrm{cm^{-1}}$ as in its original form) $> J_{\mathrm{thresh}}$ so there is expected to be an abrupt phase transition with hysteresis according to eqn (5) in the paper. In Kahn's original paper, they claimed to obtain a stable hysteresis loop of $(6 \pm 1)\,\mathrm{K}$. Our results (FIG. 1(a)) show that we would be able to reproduce their results if a fairly fast sweeping rate ($< 4\times10^2\,\mathrm{MCS/K}$) is used. But the width of the loop decreases continuously with slower sweeping rates, and the final converged value is much less than 6 K.

To demonstrate more clearly, in FIG 1(b) we depict hysteresis loop widths with respect to increasing MCS/K for another set of parameters ($\Delta H = 15\,\mathrm{kJ{\cdot}mol^{-1}}$, $\Delta S = 60\,\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$,

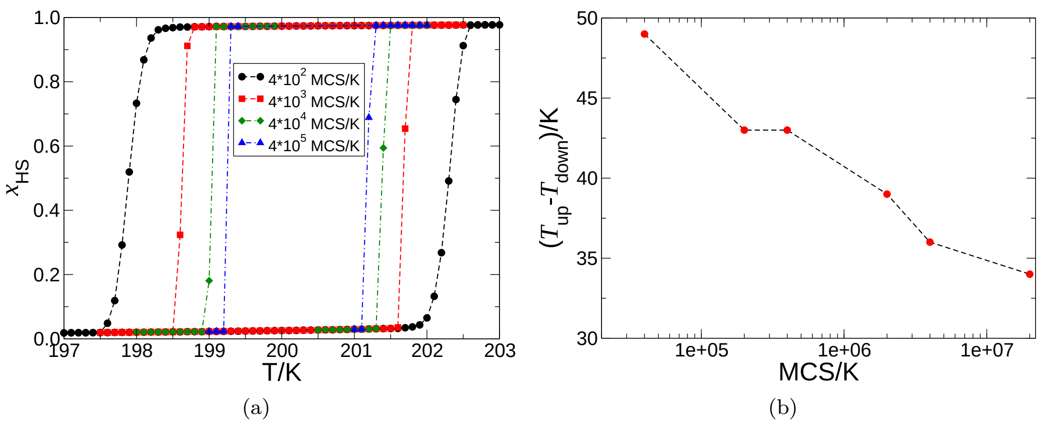

FIG. 1: (a) MC simulation of the 2D WP model using the same parameters as in ref. [1]. , in which they claimed to obtain a stable hysteresis loop with $\Delta T = 6 \pm 1\,\mathrm{K}$. (b) The variation of hysteresis loop widths with respect to the sweeping rates obtained from the 2D WP model using another set of parameters ($\Delta H = 15\,\mathrm{kJ{\cdot}mol^{-1}}$, $\Delta S = 60\,\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$, $J = 200\,\mathrm{K}$).

$J = 200\,\mathrm{K}$). This, if compared to FIG. 2 in the paper, illustrates the inability of the WP model to give a stable result even with a fairly large number of MCS per temperature point (i.e. 10^7). It is clear that there is a non-ignorable convergence problem in the WP model.

2 Simulation Based on the BAS model

Here we conduct (N, p, T)-ensemble MC simulation based on the BAS model with the same parameters as we employ in the SAB model, namely $\Delta H = 15\,\mathrm{kJ{\cdot}mol^{-1}}$, $\Delta S = 60\,\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$, $p = 1\,\mathrm{atm}$. The ratio of interaction parameters follows that in Ref. [2], i.e. $k_1 = 10k_2$. The results of transition curves and convergence properties are depicted in FIG. 2. One can see that with realistic parameters the BAS model gives similar results, including the convergence behaviour, as the SAB model does. For comparison between these two models see the paper.

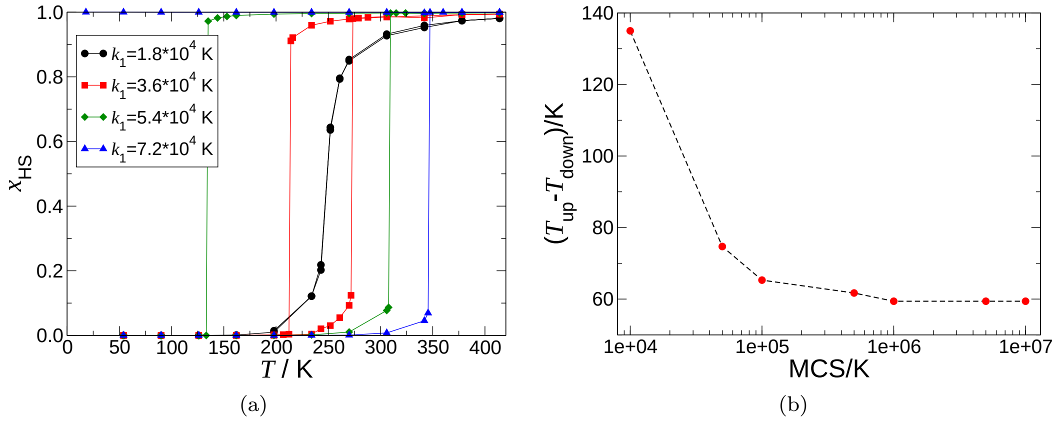

FIG. 2: Simulation results based on the BAS model. (a) Transition curves with different k's and (b) hysteresis loop widths versus sweeping rate with $k_1 = 3.6 \times 10^4\,\mathrm{K}$.

References

[1] H. Bolvin and O. Kahn. *Chem. Phys*, 192:295, 1995.

[2] Y. Konishi, H. Tokoro, M. Nishino, and S. Miyashita. *Phys. Rev. Lett.*, 100:067206, 2008.