# Appendix D

# Monte Carlo Simulations

## D.1 Equilibration

The average quantities obtained from our MC simulations should reflect the equilibrated state of the system and should thus not depend on the initial configuration with which the simulation was started. This was routinely checked by starting the simulations from different initial configurations, as well as by using different initial random number seeds. Fig. D.1 illustrates this by showing the evaluation of the total energy during a MC simulation for a 0.5 ML oxygen coverage in a (20×20) Pd(100) simulation cell. The final energy obtained after about $10^7$ MC steps does not depend on the varied initial configurations, nor on the random number seed.

While we can thus assume that the equilibrated state is reached, the initial transient equilibration period should also not enter into the averaging procedure for the thermodynamic properties. As illustrated by Fig. D.2, the initial equilibration period varies with the system temperature (and of course with O coverage). We systematically verified however that it never exceeds $\sim 5\times10^7$ MC steps (at the accuracy level of interest to our study). We therefore always employed a corresponding number of equilibration MC steps, before starting the averaging procedure for the thermodynamic properties.

## D.2 Simulation Cell for O-Pd(100)

The finite size of the simulation cell is another crucial technical factor for MC simulations, known to induce so-called *finite-size effects* [73]. Fortunately, such effects play only a minor role at the accuracy level of interest to our study, which aims more at a semi-quantitative determination of the critical temperature, rather than at a detailed investigation of the nature of the phase transition (critical exponents *etc.*) itself. Already rather small simulation cells are sufficient to determine the critical temperature for the order-disorder transition to within ±25 K. This is illustrated in Fig. D.3 by the variation of the employed order parameter and specific heat for two different O cover-

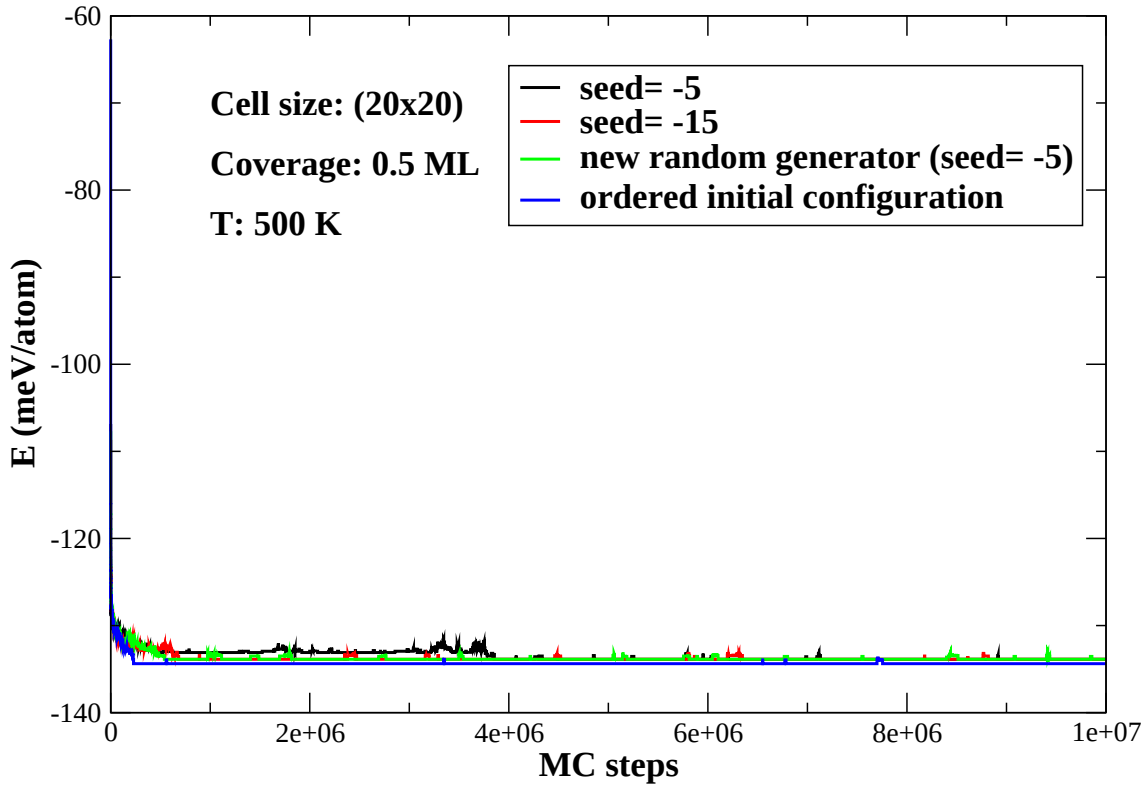


Figure D.1: Illustration of the evaluation of the total energy with Monte Carlo (MC) steps for a 0.5 ML oxygen coverage in the (20×20) simulation cell. The finally obtained value does not depend on the initial random number seed (and starting from a random initial starting configuration) or when starting from an ordered configuration.

ages at Pd(100). With increasing simulation cell size the former approaches the ideal step-function shape and the latter the $\delta$-peak shape. Using the inflection and peak temperature from both, respectively, it is clear that converged critical temperatures to within ±25 K can be obtained from simulation cells exceeding (40×40).

## D.3 Identical $T_c$ from $\Psi$ and $C_V$

Using the optimum (40 × 40) simulation cell, we identify the critical temperatures of the order-disorder transitions at 0.25 ML and 0.5 ML on Pd(100) surface by the order parameters ($\Psi_{p(2\times2)}$ in Eq. 5.23 and $\Psi_{c(2\times2)}$ in Eq. 5.27) and the specific heat. Fig. D.4 clearly shows that at low temperatures the order parameters are 1.0, which means configurations show the $p(2 \times 2)$ and $c(2 \times 2)$ order for coverages at 1/4 ML and 1/2 ML, and the specific heats are both small. When the temperatures are near the critical temperatures ($T_C$), the order parameters drop sharply, and a peak in the specific heat occurs. Increasing the temperature further, both order parameters and

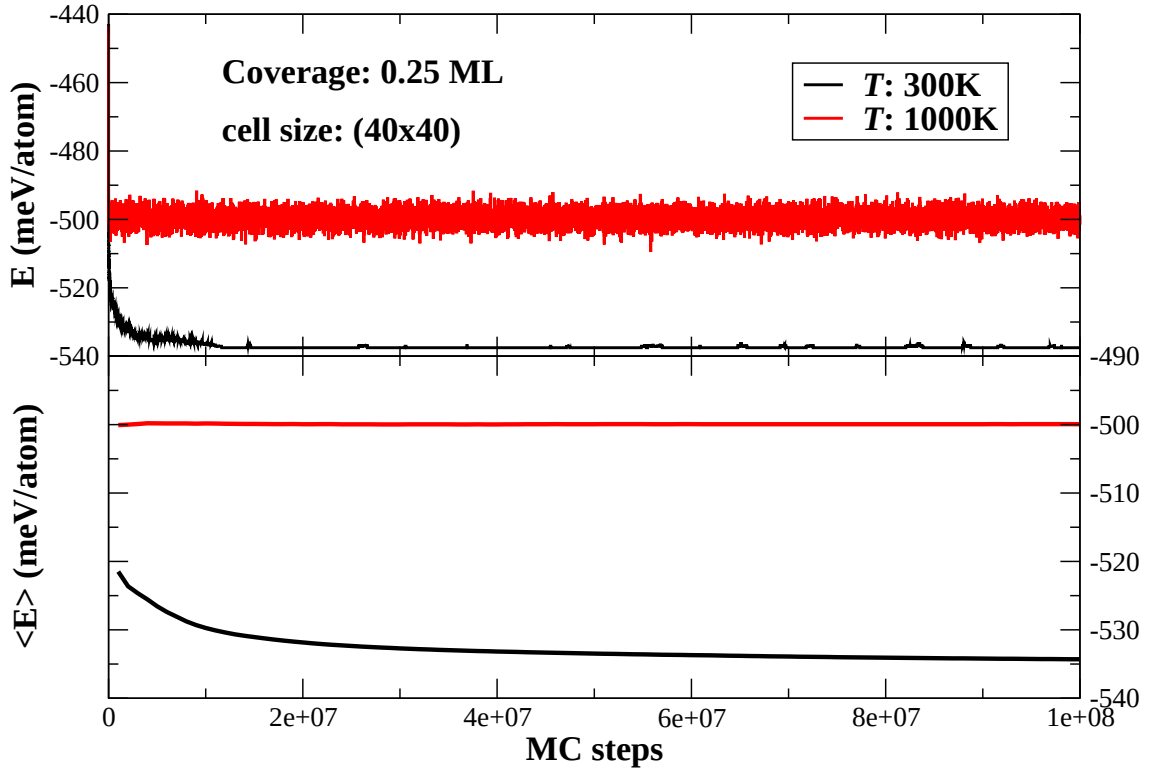


Figure D.2: E vs. MC step (top panel), and $< E >$ vs. MC step (bottom panel) for two different temperatures, 300K and 1000K.

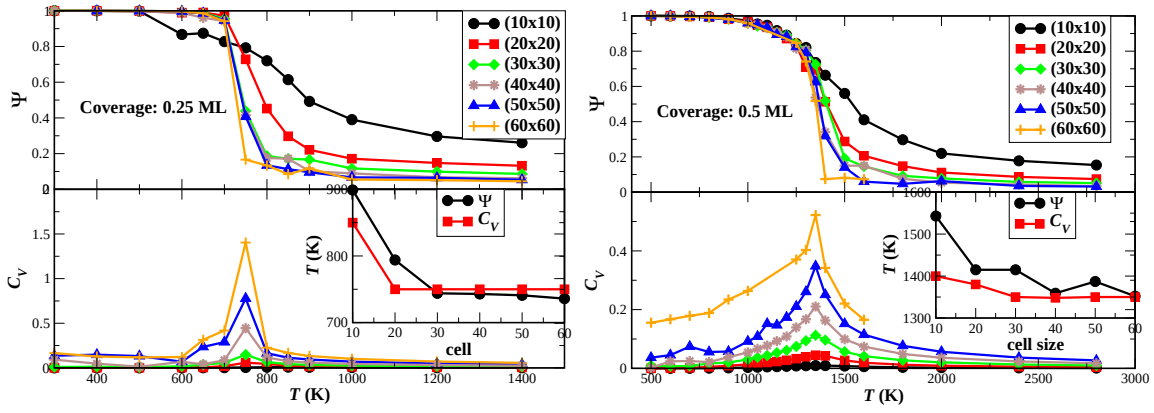


Figure D.3: Finite-size effect for two O coverages at Pd(100), $\theta$=0.25 ML (left panel) and $\theta$=0.5 ML (right panel). The critical temperatures are deduced from the order parameter (top panels) and specify heat (bottom panels). The insert panels are the $T_C$ vs. cell size.

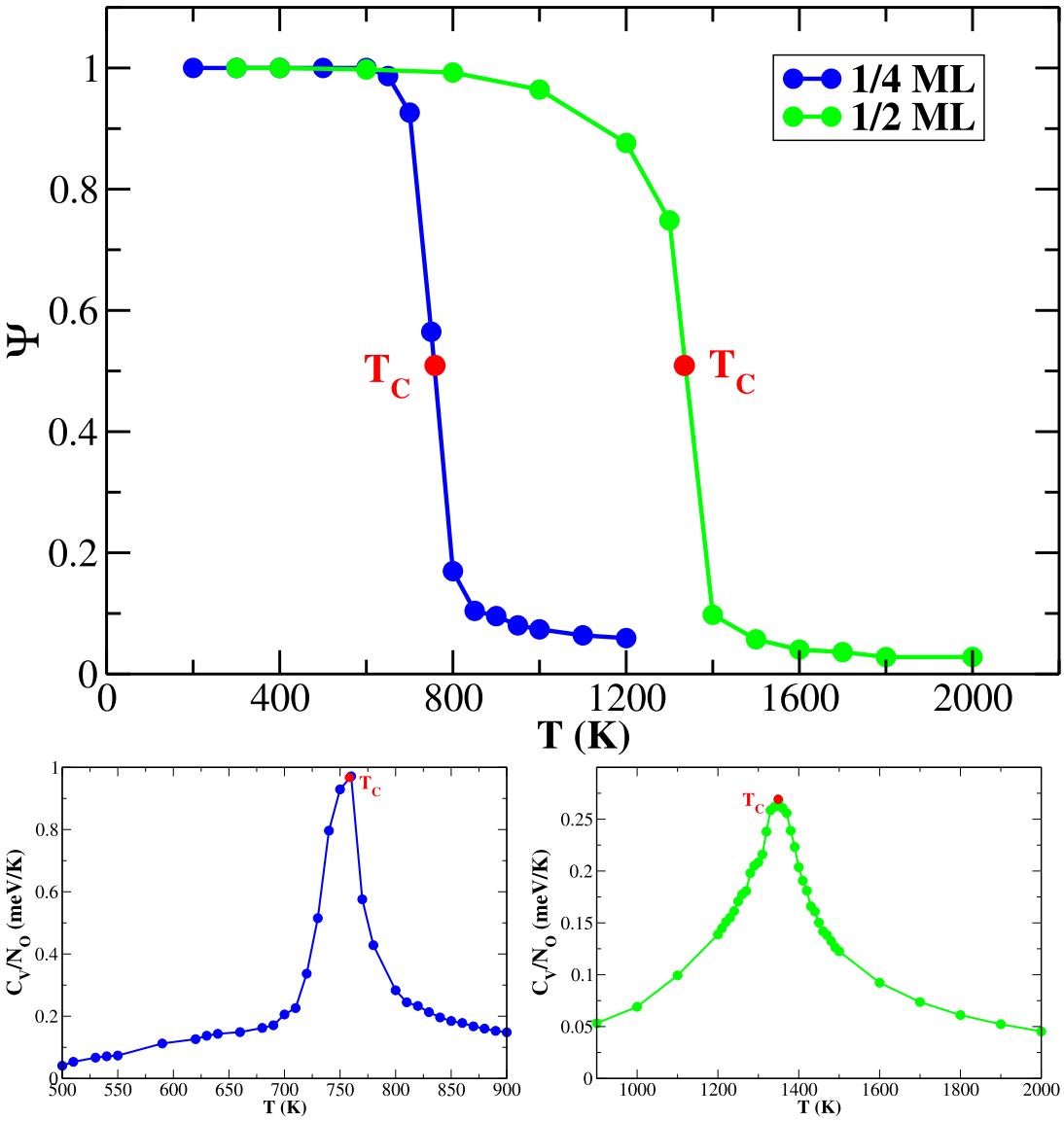


Figure D.4: Critical temperatures determined by order parameters (top panel) and specific heat (bottom panels) in a $(40 \times 40)$ simulation cell. The critical temperatures at 0.25 ML and 0.5 ML determined by the inflection points of the $p(2 \times 2)$ and $c(2 \times 2)$ order parameters, respectively, are identical to the critical temperatures determined from the peak of the specific heats to within 10 K.

specific heats are decreasing to a small value. Taking the inflection points in the order parameter curves and the peaks in the specific heat curves as the critical temperatures, we can say both of methods predict identical critical temperatures to within 10 K.

## D.4 Simulation Cell for Stepped Pd(100)

The MC simulations addressing the influence of the (111) step on the ordering behavior should simulate the limit of an isolated step. Since they still have to be simulated with periodic boundary conditions, a further series of tests needed to establish the minimum terrace width that is required to eliminate any step-step interactions. For this, we employed simulation cells of increasing terrace width ($W\times40$) with $W > 40$, *i.e.* simulation cells that exhibit one (111) step along the $y$-axis, separated by terraces of width $W$ Pd(100) unit-cells. Monitored was the specific heat for each row parallel to the (111) step separately, to identify at which distance from the step the deduced critical temperature becomes indistinguishable from that at the ideal extended Pd(100) surface.

Fig. D.5 shows this test for GCMC simulations corresponding to nominal O coverages of 0.1 and 0.15 ML at low temperatures. For two employed terrace widths we observe a rapid convergence of the critical temperature towards the value of the ideal Pd(100) surface over only 6 terrace row.

At the extended (80×40) simulation cell this behavior is exactly the same as at the (60×40) cell, just with 20 additional Pd(100) terrace rows in between. We correspondingly conclude that a (60×40) cell corresponding to terraces of 60 unit-cell width is fully sufficient to simulate the ordering behavior at "isolated" (111) steps.

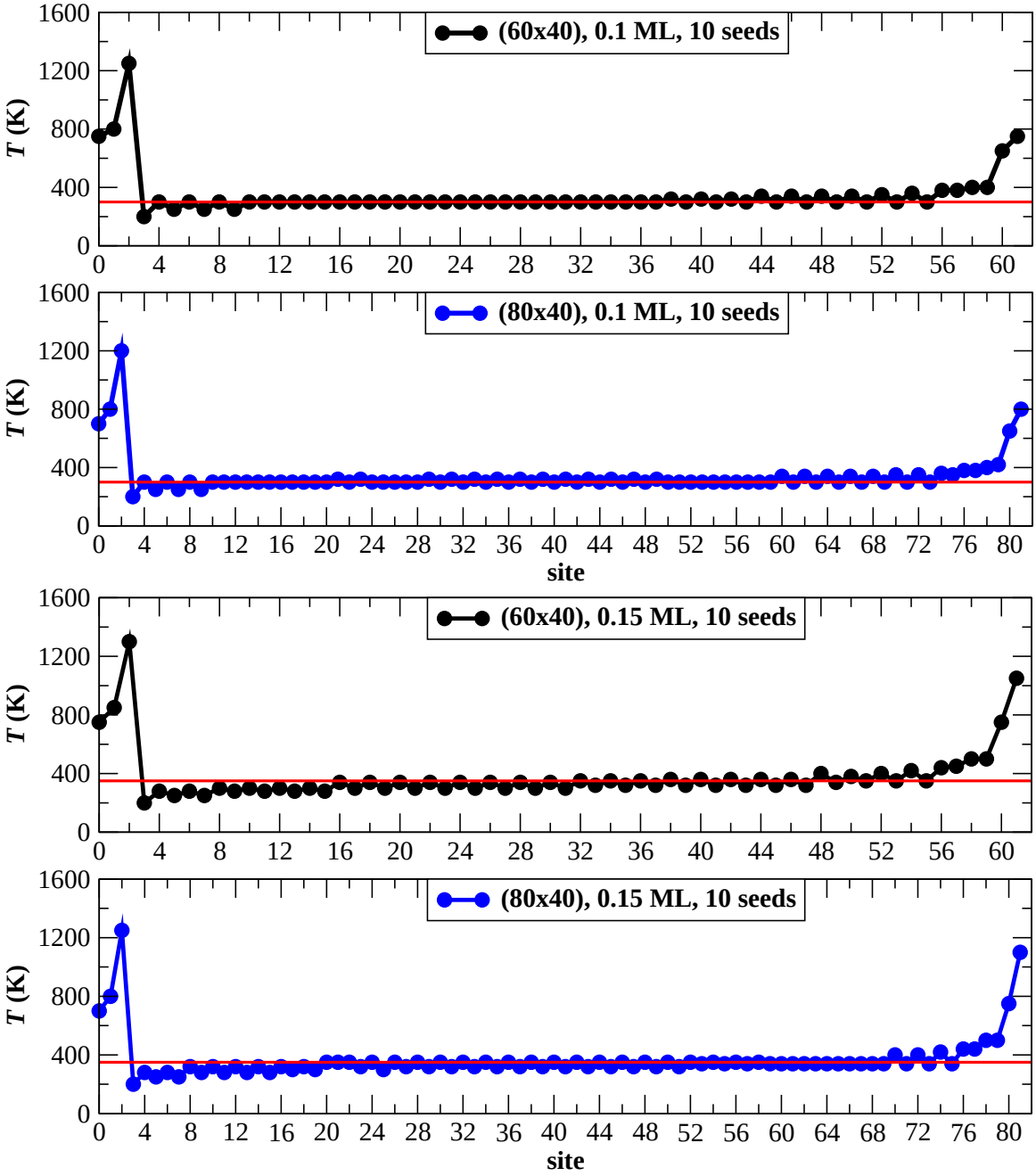


Figure D.5: Cell size tests for two coverages, $\theta$=0.1 ML (top two panels) and $\theta$=0.15 ML (bottom two panels) using two kinds of cells, $(60 \times 40)$ and $(80 \times 40)$. The additional red lines are the critical temperature for the ideal O-Pd(100) surface at the same coverages, respectively. The (111) step site Sh2 is at position 0.