APPENDIX D

CONVERGENCE OF MARKOV CHAIN MONTE CARLO CALCULATIONS

THIS appendix outlines the proof that the Markov chain Monte Carlo procedure of Section 10.3.2 always converges to the Boltzmann distribution. Recall that we start from any state of the system and repeatedly move to new states, one after another, with the probability T_{ij} of changing from state i to state j satisfying the conditions

$$\sum_j T_{ij} = 1 \tag{D.1}$$

and

$$\frac{T_{ij}}{T_{ji}} = \frac{P(E_j)}{P(E_i)}, \tag{D.2}$$

where $P(E_i)$ is the Boltzmann probability for a state with energy E_i. We wish to prove that if we continue the chain of states for long enough, the probability of being in state i will converge to $P(E_i)$.

The proof has several parts. First let us define $p_i(t)$ to be the probability that the Markov chain visits state i at step t. Then the probability that it visits state j at the next step is given by

$$p_j(t+1) = \sum_i T_{ij} p_i(t), \tag{D.3}$$

or in vector notation

$$\mathbf{p}(t+1) = \mathbf{T}\mathbf{p}(t), \tag{D.4}$$

where $\mathbf{p}$ is the vector with elements p_i and $\mathbf{T}$ is the matrix with elements T_{ji}. (Notice that it is T_{ji}—the indices have to be "backwards" to make it work out.) Thus the vector of probabilities is simply multiplied by a constant matrix on each step, which means that

$$\mathbf{p}(t) = \mathbf{T}^t \mathbf{p}(0). \tag{D.5}$$

Now let us expand the vector $\mathbf{p}(0)$ as a linear combination of the right eigenvectors $\mathbf{v}_k$ of $\mathbf{T}$ thus:

$$\mathbf{p}(0) = \sum_k c_k \mathbf{v}_k. \tag{D.6}$$

Substituting this form into Eq. (D.5), we get

$$\mathbf{p}(t) = \mathbf{T}^t \sum_k c_k \mathbf{v}_k = \sum_k c_k \lambda_k^t \mathbf{v}_k = \lambda_1^t \sum_k c_k \left(\frac{\lambda_k}{\lambda_1}\right)^t \mathbf{v}_k\,, \tag{D.7}$$

where λ_k is the eigenvector corresponding to $\mathbf{v}_k$ and λ_1 is the eigenvector of largest magnitude. Note that this argument only works if there is just a single such eigenvector, i.e., if the leading eigenvalue is unique, which we will assume for the moment to be the case. This point is discussed further below.

Now we consider what happens in the limit of long time. Dividing Eq. (D.7) throughout by λ_1^t, taking the limit $t \to \infty$, and noting that $|\lambda_k/\lambda_1| < 1$ for all k except $k = 1$ if the leading eigenvalue is unique, then all the terms in the sum will tend to zero in the limit except for the $k = 1$ term, and we are left with

$$\lim_{t\to\infty} \frac{\mathbf{p}(t)}{\lambda_1^t} = c_1 \mathbf{v}_1. \tag{D.8}$$

In other words, in the limit of long time the vector of probabilities $\mathbf{p}$ is simply proportional to the leading eigenvector of the matrix $\mathbf{T}$. Thus the probabilities always converge to the same probability distribution in the end, given by the leading eigevector. It remains to show that this leading eigenvector is, in fact, the Boltzmann distribution.

That the Boltzmann distribution is *an* eigenvector of $\mathbf{T}$ is straightforward to demonstrate. From Eq. (D.2) we have

$$\sum_j T_{ji} P(E_j) = \sum_j T_{ij} P(E_i) = P(E_i) \sum_j T_{ij} = P(E_i), \tag{D.9}$$

where we have used Eq. (D.1) in the last equality. Thus if we set $p_i = P(E_i)$ we have, in vector notation

$$\mathbf{T}\mathbf{p} = \mathbf{p}. \tag{D.10}$$

In other words, $\mathbf{p}$ is indeed an eigenvector of $\mathbf{T}$, with eigenvalue 1.

We also need to show that this is the *leading* eigenvector, which we do as follows. First of all, we note that the eigenvector of Boltzmann probabilities in Eq. (D.10) has all elements strictly positive, since the Boltzmann probabilities are strictly positive. We also note that the *left* eigenvector corresponding to eigenvalue 1 is the vector $\mathbf{1} = (1, 1, 1, \ldots)$, the vector with all elements equal

to 1. This is a result of Eq. (D.1), which in vector notation reads $\mathbf{1}^T\mathbf{T} = \mathbf{1}^T$, so that $\mathbf{1}^T$ is indeed the left eigenvector with eigenvalue 1. This result in turn implies that the (right) eigenvector of Boltzmann probabilities must be the only eigenvector that has no negative elements, since all right eigenvectors with other eigenvalues must be orthogonal to the left eigenvector $(1,1,1,\ldots)$, and the only way to be orthogonal to a vector with all elements positive is to have some negative elements.

Second, we showed in Eq. (D.8) that, upon repeated multiplication by the matrix $\mathbf{T}$, the vector $\mathbf{p}$ converges to a value proportional to the leading eigenvector of the matrix. Suppose that the starting value of $\mathbf{p}$ has all elements nonnegative. For instance, we could choose one of them to be one and the others all to be zero, which corresponds to the system being in a single definite starting state. When we multiply such a vector by $\mathbf{T}$ we will get another vector with all elements nonnegative—we must because all the elements of $\mathbf{T}$ are also nonnegative. Thus if we multiply by $\mathbf{T}$ repeatedly we will always have a vector with nonnegative elements, and hence the leading eigenvector to which we converge in the limit of long time must also have all elements nonnegative. Since, as we have said, there is only one such vector, namely the vector of Boltzmann probabilities, the vector to which we converge must be precisely the Boltzmann probabilities.

This essentially completes the proof. The only remaining detail is that one might, in principle, have more than one left/right eigenvector pair associated with eigenvalue 1, in which case our argument above that only one eigenvector has all elements positive breaks down. As we said earlier, we are assuming this not to be the case; we assume that the leading eigenvalue is unique. We have not however proved this to be the case. The reason why we haven't is that, in general, it's not true. It is entirely possible to create a reasonable matrix of transition probabilities $\mathbf{T}$ with more than one leading eigenvector. However, if the condition of ergodicity, discussed in Section 10.3.2, is enforced—the condition that every state of the system is reachable from every other by an appropriate sequence of moves—then the leading eigenvalue is normally unique, and in practice the Markov chain Monte Carlo method converges reliably to the Boltzmann distribution.