The elements on the diagonal (the no change probabilities) are on the average the largest elements of the matrix. In general, their value decreases as we proceed from the most to the least probable macrostates. The elements on the diagonal separate collisions that result in more probable macrostates (below the diagonal) from those that result in less probable macrostates (above the diagonal). Notice that the matrix is symmetric with respect to its zeros. (Macrostate IV cannot be reached from macrostate I, $p_{I-IV} = 0$ via a two-particle collision. Conversely, macrostate I cannot be reached from IV, $p_{IV-I} = 0$). For nonzero terms each probability of change to a more probable macrostate is larger than its counterpart above the diagonal pair (e.g., $p_{III-I} = 0.215 > p_{I-III} = 0.030$). Thus it is recognized that the system tends toward more probable macrostates as collisions occur. The ratio of the sum of the below-diagonal to the above-diagonal probabilities is 5.46, indicating a better than 5 to 1 tendency that any macrostate change will be toward more probable macrostates. It was pointed out above that an isolated system that has just undergone interaction is likely to be in an improbable, nonequilibrium macrostate. The transition probability matrix indicates that after relatively few collisions it is very probable that the system will have evolved to a high probability, equilibrium macrostate. Furthermore, the transition table shows that once equilibrium is achieved, a spontaneous return to nonequilibrium states is extremely improbable. Consider the following example.

Example 11. After an interaction, the 6 particle system of Table IIIA-8 is found in the least probable macrostate, VII. Determine the highest probability sequence of macrostate changes that result in the most probable macrostate, the probability of that sequence and the probability of the converse sequence.

Starting in macrostate VII the most probable result of a single collision is macrostate IV, $p_{VII-IV} = 0.864$. In row IV the most probable individual result of collision is no change, $p_{IV-IV} = 0.449$, though the system is more likely to change to one of the two accessible more probable macrostates ($p_{IV-III} + p_{IV-II} = 0.162 + 0.323 = 0.485$). The most probable change is from IV to II, $p_{IV-II} = 0.323$. In fact, macrostate II is one of the two equal probability most probable macrostates. In that sense, the very high probability of no change in macrostates II and I, $p_{II-II} = 0.713$, $p_{I-I} = 0.746$, is supportive of the maintenance of equilibrium. The change to macrostate I is the most probable change, $p_{II-I} = 0.185$. The probability of this sequence is

$$p_{VII-IV-II-I} = 0.864 \cdot 0.343 \cdot 0.185 = 0.548 \cdot 10^{-1}$$

Even though this is the most probable sequence of change, it is not very probable. No individual sequence of occurrences is. The reverse sequence is much less likely.

$$p_{I-II-IV-VII} = p_{I-II} \cdot p_{II-IV} \cdot p_{IV-VII} = 0.172 \cdot 0.042 \cdot 0.012 = 0.867 \cdot 10^{-4}$$

In fact, the system is $p_{VII-IV-II-I}/p_{I-II-IV-VII} = 6.32 \cdot 10^{2}$ times more likely to go from the least to most probable macrostate by this sequence than vice versa.

The preceding example reminds us that collisions occur in sequence. A product of the ratios of below to above the diagonal transition probabilities $\prod_{\substack{i,j \\ i \neq j}} p'_{ij}/p_{ji}$ might be more meaningfully compare than their sum. This ratio, $8.34 \cdot 10^{6}$, strongly indicates the