Here are some questions to test your mastery of the fundamentals of Boltzmann factors and partition functions used in statistical mechanics. Once you’ve mastered the material, you should be able to answer these questions without reference to your notes or textbook.

For the Boltzmann Factor and Partition Functions:

1. What is the Boltzmann Factor? How is it related to the probability of occurrence of a given microstate?

The Boltzmann Factor of a microstate \( j \) with energy \( E_j \) is \( e^{-E_j/k_B T} \), and is proportional to the probability of occurrence of a given microstate.

2. What is the partition function, \( Q \)? What information does one know if one has \( Q \)? Give some specific examples of what can be calculated from \( Q \).

\[
Q = \sum_j e^{-E_j/k_B T},
\]
from which one can calculate all thermodynamic information, include energy, pressure, heat capacity, etc.

3. Of which variables is \( Q \) a function?

\( Q = Q(N,V,T) \)

4. What is an ensemble? What physical variables are the same between members of an ensemble? How are macrostates and microstates related? How is the Boltzmann Factor related to ensembles?

An ensemble is the set of microstates that are consistent with a given macrostate. The microstates occur in the ensemble with population proportional to their likelihood of being observed in the macrostate. For example, for a macrostate specified by \( N,V,T \), the microstates are those that are consistent with those \( N,V,T \). In the \( N,V,T \) ensemble, the probability of a a given microstate is proportional to its Boltzmann factor.

5. How does the partition function of a system of identical particles differ if the particles are fermions or bosons?

The partition is a sum over the states of the total system of identical particles. For fermions all system states are antisymmetric, and for bosons all system states are symmetric.

6. What are Boltzmann statistics, and generally speaking, under what conditions do they apply? What is the partition function of a system obeying Boltzmann statistics?

Under conditions of high \( T, V \), and low \( N \), the number of states is much larger than the number of particles. In that case, the chance of two particles occupying the same
state is very low. Indistinguishability then mainly plays a role in not counting two states that are related simply by a permutation of the particle coordinates as two separate states. In that case, indistinguishability acts merely to reduce the system partition function, \( q^N \), by a factor of \( N! \) (the number of permutations), i.e. \( Q = q^N / N! \).

7. Explain qualitatively why a molecular partition function can be factored into partition functions for each degree of freedom.

Since each degree of freedom is independent, the total molecular energy can be broken down into a sum of independent contributions from each degree of freedom. This then means the Boltzmann factors, and hence the partition functions, can be factored into products of the partition functions for each degree of freedom.

In addition, you should feel comfortable doing problems like those that have been assigned in homework. Here are some additional problems you should feel comfortable doing once you’ve mastered the material.

1. Given a set of (possibly degenerate) energy levels, write down the partition function. If the sum in \( Q \) is doable (e.g. for a harmonic oscillator), do it. Be able to calculate the relative populations of different energy levels given the temperature.

Evaluate the sum \( Q = \sum_j e^{-E_j / k_B T} \) over all states \( j \), or equivalently, the sum \( Q = \sum_l g_l e^{-E_l / k_B T} \) over all levels \( l \) with degeneracy \( g_l \).

2. Given any partition function, \( Q \), calculate the thermodynamic energy, pressure and heat capacity. For instance, given \( Q \) for an ideal gas, derive the ideal gas law or its heat capacity.

\[
\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q = k_B T^2 \frac{\partial}{\partial T} \ln Q
\]

\[
C_V = \frac{\partial \langle E \rangle}{\partial T}
\]

\[
\langle P \rangle = k_B T \frac{\partial}{\partial V} \ln Q
\]

For an ideal gas, \( Q = V^N \) * terms not involving \( V \), and so

\[
\langle P \rangle = k_B T \frac{\partial}{\partial V} [N \ln V + \text{terms not involving } V] = Nk_B T / V
\]

\[
\langle P \rangle V = Nk_B T
\]
3. Prove that $Q$ for a system of distinguishable particles is the product of the partition functions of the individual particles. As a corollary, explain why $Q=q^N$ if the $N$ particles are identical, where $q$ is the partition function of an individual particle.

For two identical particles we have $Q = \sum_{i,j} e^{-\beta(E_i + E_j)} = \sum_i e^{-\beta E_i} \sum_j e^{-\beta E_j} = q^2$, and so by extension of the same argument, for $N$ identical but distinguishable particles, $Q=q^N$.

4. Given a system of identical particles with a finite number of states, list the states of the system if the particles are a) fermions or b) bosons.

As an example, for two particles, the set of states for the system of two-particles can be thought of as a square grid. The fermion states are all those above the diagonal, and the boson states are all those above and including the diagonal.