# 4.2: The Relation of State Functions to the Partition Function

## Entropy and the Partition Function

We recall that we already computed internal energy $u$ and heat capacity $c_V$ at constant volume from the system partition function $z$ (Section [section:u_and_cv_from_z]). For a canonical system ($V = \text{const.}$), which is by definition at thermal equilibrium (reversible), we can identify $q_\text{rev}$ in Equation ??? with[14]

$$\mathrm{d}q_\text{rev} = c_V \mathrm{d}T \ . \tag{4.2.1}$$

Definite integration with substitution of $c_V$ by Equation ??? gives ,

$$s - s_0 = \int_0^T \frac{c_V}{T'} \mathrm{d}T' = \int_0^T \frac{1}{T'} \frac{\partial}{\partial T'} \left( k_\text{B} T'^2 \frac{\partial \ln z}{\partial T'} \right)_V \mathrm{d}T' \tag{4.2.2}$$

$$= \int_0^T \frac{1}{T'} \left[ k_\text{B} T'^2 \left( \frac{\partial^2 \ln z}{\partial T'^2} \right)_V + 2 k_\text{B} T' \left( \frac{\partial \ln z}{\partial T'} \right)_V \right] \mathrm{d}T' \tag{4.2.3}$$

$$= k_\text{B} \int_0^T T' \left( \frac{\partial^2 \ln z}{\partial T'^2} \right)_V \mathrm{d}T' + 2 k_\text{B} \int_0^T \left( \frac{\partial \ln z}{\partial T'} \right)_V \mathrm{d}T' \ . \tag{4.2.4}$$

Partial integration provides

$$s - s_0 = k_\text{B} T \left( \frac{\partial \ln z}{\partial T} \right)_V - k_\text{B} \int_0^T \left( \frac{\partial \ln z}{\partial T'} \right)_V \mathrm{d}T' + 2 k_\text{B} \int_0^T \left( \frac{\partial \ln z}{\partial T'} \right)_V \mathrm{d}T' \tag{4.2.5}$$

$$= k_\text{B} T \left( \frac{\partial \ln z}{\partial T} \right)_V + k_\text{B} \ln z \Big|_0^T \tag{4.2.6}$$

$$= \frac{u}{T} + k_\text{B} \ln z - k_\text{B} (\ln z)_{T=0} \ , \tag{4.2.7}$$

where we have used Equation ??? to substitute the first term on the right hand side of Equation 4.2.6. If we assume that $\lim_{T \to 0} u/T = 0$, the entropy at an absolute temperature of zero can be identified as $s_0 = k_\text{B} (\ln z)_{T=0}$. If there are no degenerate ground states, $s_0 = 0$ in agreement with Nernst's theorem (Third Law of Thermodynamics), as will be discussed in Section [subsection:z_accessible]. Thus, by associating $u = 0$ with $T = 0$ we obtain

$$s = \frac{u}{T} + k_\text{B} \ln z = k_\text{B} \left[ \left( \frac{\partial \ln z}{\partial \ln T} \right)_V + \ln z \right] \ . \tag{4.2.8}$$

We see that under the assumptions that we have made the entropy can be computed from the partition function. In fact, there should be a unique mapping between the two quantities, as both the partition function and the entropy are state functions and thus must be uniquely defined by the state of the system.

We now proceed with computing constant $k$ in the mathematical definition of Boltzmann entropy, Equation ???. By inserting Equation ??? into Equation ??? we have

$$s = k \left( N \ln N - \sum_{i=0}^{r-1} N_i \ln N_i \right) \ . \tag{4.2.9}$$

We have neglected the term $r$ on the right-hand side of Equation ???), as is permissible if the number $N$ of particles is much larger than the number $r$ of energy levels. Furthermore, according to Equation ???) and the definition of the partition function, we have $N_i = N e^{-\epsilon_i / k_\text{B} T} / Z$. Hence,

$$s = k \left[ N \ln N - N \sum_{i=0}^{r-1} \frac{e^{-\epsilon_i/k_{\mathrm{B}}T}}{Z} \ln N \left( \frac{e^{-\epsilon_i/k_{\mathrm{B}}T}}{Z} \right) \right] \tag{4.2.10}$$

$$= k \left[ N \ln N - N \sum_{i=0}^{r-1} \frac{e^{-\epsilon_i/k_{\mathrm{B}}T}}{Z} \ln N + N \sum_{i=0}^{r-1} \frac{e^{-\epsilon_i/k_{\mathrm{B}}T}}{Z} \ln Z + N \sum_{i=0}^{r-1} \frac{e^{-\epsilon_i/k_{\mathrm{B}}T}}{Z} \cdot \frac{\epsilon_i}{k_{\mathrm{B}}T} \right] \tag{4.2.11}$$

$$= k \left[ N \ln N - N \ln N + N \ln Z + \frac{N}{k_{\mathrm{B}}T} \frac{\sum_{i=0}^{r-1} \epsilon_i e^{-\epsilon_i/k_{\mathrm{B}}T}}{Z} \right] , \tag{4.2.12}$$

where we have used the definition of the partition function of going from Equation 4.2.11 to ???. Using Equation ??? for substitution in the last term on the right-hand side of Equation 4.2.12), we find

$$s = k \left[ N \ln Z + \frac{u}{k_{\mathrm{B}}T} \right] . \tag{4.2.13}$$

Comparison of Equation 4.2.13 with Equation 4.2.8 gives two remarkable results. First, the multiplicative constant $k$ in Boltzmann's entropy definition can be identified as $k = k_{\mathrm{B}} = R/N_{\mathrm{Av}}$. Second, for the system of $N$ identical, distinguishable classical particles, we must have

$$z_{\mathrm{dist}} = Z^N . \tag{4.2.14}$$

In other words, the partition function of a system of $N$ identical, distinguishable, non-interacting particles is the $N^{\mathrm{th}}$ power of the molecular partition function.

It turns out that Equation 4.2.14 leads to a contradiction if we apply it to an ideal gas. Assume that we partition the system into two subsystems with particle numbers $N_{\mathrm{sub}} = N/2$. The internal-energy dependent term in Equation 4.2.13 obviously will not change during this partitioning. For the partition-function dependent term we have $N \ln Z$ for the total system and $2(N/2) \ln Z'$ for the sum of the two subsystems. The molecular partition function in the subsystems differs, because volume available to an individual particle is only half as large as in the total system. For the inverse process of unifying the two subsystems we would thus obtain a mixing entropy, although the gases in the subsystems are the same. This appearance of a mixing entropy for two identical ideal gases is called the **Gibbs paradox**. The Gibbs paradox can be healed by treating the particles as indistinguishable. This reduces the statistical weight $\Omega$ by $N!$ for the total system and by $(N/2)!$ for each subsystem, which just offsets the volume effect. Hence, for an ideal gas we have

$$z_{\mathrm{indist}} = \frac{1}{N!} Z^N . \tag{4.2.15}$$

It may appear artificial to treat classical particles as indistinguishable, because the trajectory of each particle could, in principle, be followed if they adhere to classical mechanics equations of motion, which we had assumed. Note, however, that we discuss a macrostate and that we have explicitly assumed that we cannot have information on the microstates, i.e., on the trajectories. In the macrostate picture, particles in an ideal gas are, indeed, indistinguishable. For an ideal crystal, on the other hand, each particle could be individually addressed, for instance, by high resolution microscopy. In this case, we need to use Equation 4.2.14.

## Helmholtz Free Energy

Helmholtz free energy (*German:* Freie Energie) $f$ is defined as

$$f = u - Ts . \tag{4.2.16}$$

This equation has a simple interpretation. From phenomenological thermodynamics we know that the equilibrium state of a closed systems corresponds to a minimum in free energy. Among all macrostates with the same energy $u$ at a given temperature $T$, the equilibrium state is the one with maximum entropy $s$. Furthermore, using Equation 4.2.8 we have

$$f = u - T \left( u/T + k_{\mathrm{B}} \ln z \right) \tag{4.2.17}$$

$$= -k_{\mathrm{B}} T \ln z . \tag{4.2.18}$$

We note that this value of $f$, which can be computed from only the canonical partition function and temperature, corresponds to the global minimum over all macrostates. This is not surprising. After all, the partition function was found in a maximization of the probability of the macrostate.

## Gibbs Free Energy, Enthalpy, and Pressure

All ensembles that we have defined correspond to equilibrium states at constant volume. To make predictions for processes at constant pressure or to compute enthalpies $h = u + pV$ and Gibbs free energies $g = f + pV$ we need to compute pressure from the partition function. The simplest way is to note that $p = -(\partial f / \partial V)_{T,n}$. With Equation 4.2.18 it then follows that

$$p = k_{\mathrm{B}} T \left( \frac{\partial \ln z}{\partial V} \right)_{T} , \tag{4.2.19}$$

where we have skipped the lower index $n$ indicating constant molar amount. This is permissible for the canonical ensemble, where the number of particles is constant by definition. From Equation 4.2.19 it follows that

$$pV = k_{\mathrm{B}} T \left( \frac{\partial \ln z}{\partial \ln V} \right)_{T} \tag{4.2.20}$$

and

$$h = u + pV = k_{\mathrm{B}} T \left[ \left( \frac{\partial \ln z}{\partial \ln T} \right)_{V} + \left( \frac{\partial \ln z}{\partial \ln V} \right)_{T} \right] . \tag{4.2.21}$$

Connoisseurs will notice the beautiful symmetry of this equation.

With Equation 4.2.19 we can also compute **Gibbs free energy** (*German:* freie Enthalpie),

$$g = f + pV = -k_{\mathrm{B}} T \left[ \ln z - \left( \frac{\partial \ln z}{\partial \ln V} \right)_{T} \right] . \tag{4.2.22}$$