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# Heat and Work, the First Law of Thermodynamics from the Boltzmann POV\*

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The First Law of Thermodynamics is discussed in terms of the Boltzmann distribution.

FIG. 1. The Boltzmann tombstone in Vienna



## I. REVIEW

We know that

$$S = k_B \ln W_{max} \quad (1)$$

(we've added the subscript "B" to remind us that this constant is a named one!) where

$$W_{max} = \frac{N!}{\prod_i n_i!} \quad (2)$$

in which the energy level occupation numbers are those which describe equilibrium, i.e.,

$$n_i^\otimes = \frac{N e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}} = \frac{N}{Z} e^{-\beta \epsilon_i} \quad (3)$$

As usual, using Stirling's approximation, we have

$$\ln W_{max} = N \ln N - N - \sum_i \left( n_i^\otimes \ln n_i^\otimes - n_i^\otimes \right) \quad (4)$$

where we note in passing that

$$\sum_i n_i = N$$

(whether we are in the equilibrium state or not) results in a fortuitous cancellation.

Substituting the equilibrium populations (Equation 3) into the occupation numbers of Equation 4 we obtain

$$\ln W_{max} = N \ln N - \sum_i \left( \frac{N e^{-\beta \epsilon_i}}{Z} \ln \frac{N e^{-\beta \epsilon_i}}{Z} \right) \quad (5)$$

which is

$$\ln W_{max} = N \ln N - \frac{N}{Z} \sum_i \left( e^{-\beta \epsilon_i} (\ln N - \beta \epsilon_i - \ln Z) \right) \quad (6)$$

$$\ln W_{max} = \frac{N}{Z} \beta \sum_i \epsilon_i e^{-\beta \epsilon_i} + N \ln Z$$

where, of course,

$$Z \equiv \sum_i e^{-\beta \epsilon_i}$$

so that

$$S = k_B [\beta E + N \ln Z]$$

where, we know that  $\beta = \frac{1}{k_B T}$ . Therefore, cross multiplying by  $T$  we have

$$TS = E + N k_B T \ln Z$$

or

$$E - TS = -N k_B T \ln Z \equiv A$$

This fundamental identification of the Helmholtz Free Energy with the partition function shows that  $A$  (and  $Z$ ) are functions of temperature and volume.

\* point of view

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### A. aside

Now, for a one dimension gas (where  $L$  will serve instead of  $V$ ), we know that the energy levels are given by the quantum mechanical formula

$$\epsilon_i = \frac{i^2 \hbar^2 \pi^2}{2mL^2}$$

Since the energy levels are themselves functions of the volume (here length,  $L$ ), it is apparent that when one substitutes these energy levels into the partition function that one generates a function of  $T$  and  $L$  (or  $V$ , if you will):

$$Z = \sum_i e^{-\frac{i^2 \hbar^2 \pi^2}{2ml^2 k_B T}}$$

Further, as all elementary treatments show, this partition function leads to the average thermal energy being  $E = (1/2)Nk_B T$ , where, had we done the derivation in three dimensions, we would have had  $(3/2)Nk_B T$ . This, of course, is a triumph of the statistical mechanical theory.

## II. THE MAIN ARGUMENT

But, from thermodynamics, we had

$$dE = dq + dw$$

and from statistical thermodynamics we now have

$$E = \sum_i n_i^\otimes \epsilon_i$$

and we see that there are two ways to change the energy in this last expression, changing the energy levels themselves, or changing the occupation numbers. Thus

$$dE = \sum_i \{dn_i^\otimes \epsilon_i + n_i^\otimes d\epsilon_i\}$$

The first term corresponds to heat ( $dq$ ), and the second term corresponds to work ( $dw$ ). What a spectacular clarification. Keeping systems in their individual energy levels but allowing those levels to shift corresponds to external work of some kind. Keeping the energy levels fixed and shifting the populations of those energy levels corresponds to heating (or cooling). Adiabatic processes correspond to processes in which the populations are maintained constant. Heat addition (or subtraction) results in population changes, while work (either the system performing it or having it performed on the system) results in changes in the energy levels themselves.

FIG. 2. A cartoon version of the difference between work and heat from the Boltzmann POV

