Boltzmann without Lagrange *

C. W. David

April 22, 2005

In a wonderful paper, F. T. Wall showed that one can avoid Lagrange multipliers in deriving the Boltzmann distribution [1]. This paper rephrases Wall's arguments slightly, offering what appears to be a simpler approach to part of his derivation.

We start with the elementary definition that $A = E - TS$, and notice that the thermodynamic probability of a state characterized by "occupation" numbers $\{n_i\}$ for the number of particles with energy E_i in a given (not necessarily optimal) distribution (complection) is

$$\Omega \equiv N! \prod_i \left(\frac{g_i^{n_i}}{n_i!} \right) \tag{1}$$

where g_i is the degeneracy of the i^{th} state. For non-degenerate energy levels, the more common form of this probability expression is:

$$\Omega = \frac{N!}{\prod_i n_i!}$$

In Figure 1 we have the non-degenerate ($g_i = 1 \forall i$) [2] distribution which would have the thermodynamic probability of

$$\Omega \equiv 5! \left(\frac{1^1}{1!} \right)_{i=1} \left(\frac{1^1}{1!} \right)_{i=2} \left(\frac{1^2}{2!} \right)_{i=3} \left(\frac{1^1}{1!} \right)_{i=4}$$

In the lower half of Figure 1 we have a degenerate case, which would lead to

$$\Omega \equiv 5! \left(\frac{2^1}{1!} \right)_{i=1} \left(\frac{1^1}{1!} \right)_{i=2} \left(\frac{3^2}{2!} \right)_{i=3} \left(\frac{2^1}{1!} \right)_{i=4}$$

*thermo6.tex

[1] F. T. Wall, Proc. Nat. Acad. Sci, 68, 1720 (1971).

[2] The symbol $\forall$ stands for "for all".

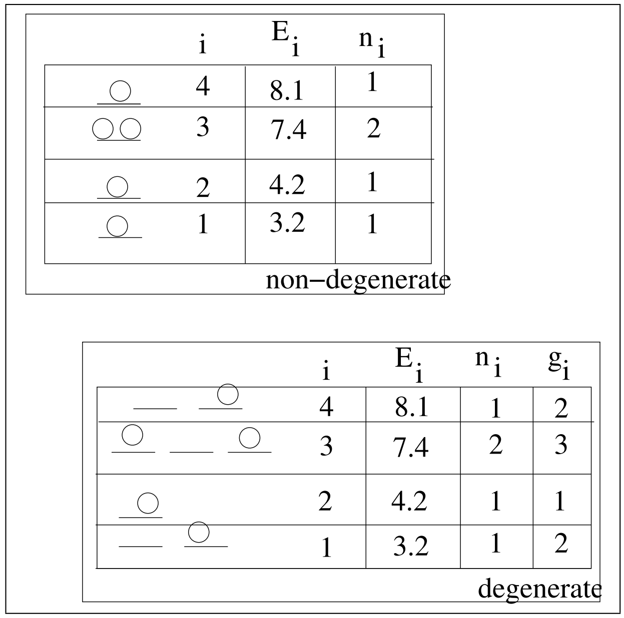

Figure 1: Distributions of particles amongst energy levels.

We assume that there is one (and only one) distribution $\{n_i\}$which maximizes Ω. This distribution (complection) is denoted as $\{n_i^\star\}$, where each energy level's occupancy number is optimal to make Ω the biggest possible value. Said another way,

$$\Omega(\{n_i\}) \rightarrow \Omega^{max}(\{n_i^\star\})$$

This will mean that any change in occupancy numbers (from those of the thermodynamically realized state) must result in lowering Ω which is the thrust of the argument which follows. Remember, one has to change at least two occupancy numbers, one going up, the other going down, in order to conserve the number of particles in the system

$$\sum_i n_i = N = \sum_i n_i^\star$$

whether we are "at equilibrium" or not.

The total energy of a system (for any complection) such as this is given by

$$E = \sum_i n_i \tag{2}$$

including the optimal complection which maximizes the thermodynamic probability (Ω). The entropy of the system is

$$S = k\ell n \Omega^{max} \tag{3}$$

where, for "boltzons", Equation 1 holds (this is different for Fermi-Dirac and Bose-Einstein particles).

Then the Helmholtz energy would be

$$A = E - TS$$

which translates into by substituting Equation 2 and Equation 3 into the defining equation yielding

$$B = \sum_i n_i E_i - T\left[k\ell n\left(\prod_i\left(\frac{g_i^{n_i}}{n_i!}\right)\right]\right) \tag{4}$$

which, when $\{n_i\} \rightarrow \{n_i^\star\}$ then $B \rightarrow A$, i.e.,

$$A = \sum_i n_i^\star E_i - T\left[k\ell n\left(\prod_i\left(\frac{g_i^{n_i^\star}}{n_i^\star!}\right)\right]\right) \tag{5}$$

Following Wall, we note that the first (energy) term can be rewritten as

$$E = \sum_i n_i^\star E_i = -kT\ell n\left(\prod_i e^{-n_i^\star E_i/kT}\right) = -kT\sum_i\left(\ell n e^{-n_i^\star E_i/kT}\right) = -kT\sum_i\left(-\frac{n_i^\star E_i}{kT}\right)$$

(where the kT cancels) so substituting this into the r.h.s. of Equation 5 for A gives us

$$A = -kT\ell n\left(\prod_i e^{-n_i^\star E_i/kT}\right) - kT\ell n\left(\prod_i\left(\frac{g_i^{n_i^\star}}{n_i^\star!}\right)\right)$$

which can be re-written in the form

$$B = -kT\ell n\left(N!\prod_i\left(\frac{\left(g_i e^{-E_i/kT}\right)^{n_i}}{n_i!}\right)\right)$$

so that

$$A = -kT\ell n\left(N!\prod_i\left(\frac{\left(g_i e^{-E_i/kT}\right)^{n_i^\star}}{n_i^\star!}\right)\right)$$

since the Helmholtz Free Energy, is only defined at thermodynamic equilibrium, so we need a different function, call it B, which will approach A as $\{n_i\} \rightarrow \{n_i^\star\}$. To minimize B by choices of $\{n_1\}$ (i.e., different complections) is our problem. Following Wall, we simplify the notation, defining

$$g_i e^{-E_i/kT} \rightarrow f_i \tag{6}$$

which allows us to write

$$A = -kT\ell n\left(N!\prod_i\left(\frac{f_i{}^{n_i^\star}}{n_i^\star!}\right)\right)$$

Consider levels 7 and 14. Then

$$A = -kT\ell n\left[N!\prod_{i=1}^{i=6}\left(\frac{f_i{}^{n_i^\star}}{n_i^\star!}\right)\otimes\frac{f_7^{n_7^\star}}{n_7^\star!}\otimes\prod_{i=8}^{i=13}\left(\frac{f_i{}^{n_i^\star}}{n_i^\star!}\right)\otimes\frac{f_{14}^{n_{14}^\star}}{n_{14}^\star!}\otimes\prod_{i=15}^{i=\infty}\left(\frac{f_i{}^{n_i^\star}}{n_i^\star!}\right)\right]$$

Our argument is, if $n_7^\star$ increases by one, and $n_{14}^\star$ compensates by decreasing by one, can we show that the Helmoholtz Free Energy goes up (i.e., away from the minimum) or, if we were at a minimum, is zero?

$$\frac{A_{before}-A_{after}}{-kT} = \ell n\left(\frac{\left(\frac{f_7^{n_7^\star}}{n_7^\star!}\right)}{\left(\frac{f_7^{n_7^\star+1}}{(n_7^\star+1)!}\right)}\frac{\left(\frac{f_{14}^{n_{14}^\star}}{n_{14}^\star!}\right)}{\left(\frac{f_{14}^{n_{14}^\star-1}}{(n_{14}^\star-1)!}\right)}\right)$$

We note that $(n_7^\star+1)! = (n_7^\star+1)n_7^\star!$ and

$$(n_{14}^\star-1)! = \frac{n_{14}^\star!}{n_{14}^\star}$$

so, we have:

$$\frac{A_{before}-A_{after}}{-kT} = \ell n\left(\frac{\left(\frac{f_7^{n_7^\star}}{n_7^\star!}\right)}{\left(\frac{f_7^{n_7^\star+1}}{(n_7^\star+1)!}\right)}\frac{\left(\frac{f_{14}^{n_{14}^\star}}{n_{14}^\star!}\right)}{\left(\frac{f_{14}^{n_{14}^\star-1}}{(n_{14}^\star-1)!}\right)}\right) \sim \ell n\left(\frac{f_{14}(n_7^\star+1)}{f_7 n_{14}^\star}\right)$$

If A, the Helmholtz Free Energy were a function of n, and n was a continuous rather than a discrete variable, then $\frac{dA}{dn} \rightarrow 0$ would indicate a value of n, say $n^\star$ where A had a zero derivative (possible maximum, possible minimum, etc.). Converting the derivative to a Δ, i.e., $\frac{\Delta A}{\Delta n} \rightarrow 0$ and remembering that Δn can, at least, be one, we could require that at the optimal values of n ($n^\star$), $\frac{\Delta A}{1} = 0$. Said another way (for large occupation numbers, $n^\star \pm 1 \rightarrow n^\star$):

$$\frac{\Delta A}{\Delta n} = \frac{\Delta A}{1} \rightarrow \frac{A_{before} - A_{after}}{-kT} \sim \ell n \left(\frac{f_{14}}{n^\star_{14}}\right) - \ell n \left(\frac{f_7}{n^\star_7}\right) \rightarrow 0$$

but this must be zero, i.e., $\frac{\Delta A}{\Delta n} \rightarrow 0$ at the minimum of B($\{n\}$). If the natural logs have to be equal, then so do their arguments, and we have [3]

$$\frac{f_{14}}{n^\star_{14}} = \frac{f_7}{n^\star_7}$$

or, in general,

$$\frac{f_1}{n^\star_1} = \frac{f_2}{n^\star_2} = \frac{f_3}{n^\star_3} = \cdots \equiv \frac{1}{a}$$

where a is a (to be determined) constant. Then using Equation 6, we have

$$n^\star_i = af_i = ag_i e^{-E_i/kT}$$

which is the result sought!

[3] Alternatively,

$$\ell n \left(\frac{f_{14}}{n^\star_{14}}\right) - \ell n \left(\frac{f_7}{n^\star_7}\right) = \ell n \left(\frac{f_{14} n^\star_7}{n^\star_{14} f_7}\right) = 0$$

so

$$\frac{f_{14} n^\star_7}{n^\star_{14} f_7} = 1$$

or

$$\left(\frac{f_{14}}{n^\star_{14}}\right)\left(\frac{n^\star_7}{f_7}\right) = 1$$

or

$$\frac{\left(\frac{f_{14}}{n^\star_{14}}\right)}{\left(\frac{f_7}{n^\star_7}\right)} = 1$$