Reino W. Hakala
Howard University
Washington, D. C.

Alternative Derivations of the Boltzmann Distribution Law

In a previous article,[1] a derivation was given of the Boltzmann distribution law which had the main virtue that the approximation used (in place of the usual Stirling approximation) was introduced at the very end of the derivation instead of at the beginning as is customary. This derivation involved the proof of the relationship

$$1 + {}^1/_2 + {}^1/_3 + \ldots + 1/N_i = \sum_{x=1}^{N_i} \frac{1}{x} \approx \ln N_i$$

which holds for very large values of N_i. Another way to find this relationship is as follows:

Since

$$\Delta x = 1 \text{ in } \sum_{x=1}^{N_i} \frac{1}{x}$$

and as

$$\frac{\Delta x}{N_i} = \Delta\left(\frac{x}{N_i}\right)$$

it follows that

$$\sum_{x=1}^{N_i} \frac{1}{x} = \sum_{x=1}^{N_i} \left(\frac{1}{x}\right) \Delta x = \sum_{x=1}^{N_i} \left(\frac{N_i}{x}\right)\left(\frac{\Delta x}{N_i}\right) = \sum_{x=1}^{N_i} \left(\frac{N_i}{x}\right) \Delta\left(\frac{x}{N_i}\right)$$

Keeping $\Delta x = 1$,

$$\Delta\left(\frac{x}{N_i}\right) = \frac{\Delta x}{N_i} \rightarrow 0 \text{ as } N_i \rightarrow \infty$$

Hence

$$\lim_{N_i \rightarrow \infty} \sum_{x=1}^{N_i} \frac{1}{x} = \lim_{\Delta (x/N_i) \rightarrow 0} \sum_{x=1}^{N_i} \left(\frac{N_i}{x}\right) \Delta\left(\frac{x}{N_i}\right)$$
$$= \int_1^{N_i} \left(\frac{N_i}{x}\right) d\left(\frac{x}{N_i}\right) = \int_0^{\ln N_i} d \ln\left(\frac{x}{N_i}\right)$$
$$= \ln N_i \text{ } (= \infty \text{ at the limit})$$

For very large values of N_i, therefore,

$$\sum_{x=1}^{N_i} \frac{1}{x} \approx \ln N_i$$

The earlier approach offers some practice with series; the present approach illustrates a proper technique for the approximation of series by integrals.

Wyatt[2] has pointed out that the essence of the author's previous article was the demonstration that

$$\delta \ln N_i! \approx \ln N_i \delta N_i$$

when N_i is large. If, however, this substitution is made where $\delta \ln N_i!$ first makes its appearance, an approximation is thereby introduced at an earlier stage of the derivation—before the use of Lagrange's method of undetermined multipliers instead of several steps after. Nevertheless, Wyatt's modification, involving an elegant proof of the above approximation, is quite beautiful. It seems worth while in this connection to show that Stirling's approximation can also be used at this particular stage of the derivation.

Following the earlier derivation, it is first proved that

$$\sum \delta \ln N_i! + a\sum \delta N_i + b\Sigma e_i \delta N_i = 0$$

This relationship was not explicitly stated in the previous article although use was directly made of it. Then Stirling's approximation is employed to derive the above approximation for $\delta \ln N_i!$:

$$\begin{aligned} \delta \ln N_i! &\approx \delta(N_i \ln N_i - N_i) \\ &\approx \delta N_i \ln N_i - \delta N_i \\ &\approx N_i \delta \ln N_i + \ln N_i \delta N_i - \delta N_i \\ &\approx \delta N_i + \ln N_i \delta N_i - \delta N_i \\ &\approx \ln N_i \delta N_i \end{aligned}$$

Substitution of this result into the previous equation then gives the approximate relationship

$$\sum (\ln N_i + a + be_i)\delta N_i \approx 0$$

which, assuming independent, non-zero variations of the occupancies δN_i ($i = 0, 1, 2, 3, \ldots$) leads to

$$\ln N_i + a + be_i \approx 0$$

or

$$N_i \approx \exp(-a - be_i)$$

which is one form of the Boltzmann distribution law.

If this approach utilizing Stirling's approximation is preferred, use can be made of Wall's simple geometric proof[3] of Stirling's approximation which, in algebraic form, is essentially as follows:

$$\begin{aligned} \ln N! &= \ln(1 \cdot 2 \cdot 3 \ldots N) \\ &= \ln 1 + \ln 2 + \ldots + \ln N \\ &= \sum_{x=1}^{N} \ln x = \sum_{x=1}^{N} (\ln x)\, \Delta x \\ &\approx \int_1^N \ln x \, dx = N \ln N - N + 1 \\ &\approx N \ln N - N; \; N \gg 1 \end{aligned}$$

To prove that

$$\int \ln x \, dx = x \ln x - x + c$$

[1] Hakala, R. W., J. Chem. Educ., **38**, 33 (1961).
[2] Wyatt, P. A. H., J. Chem. Educ., **39**, 27 (1962).

[3] Wall, F. T., "Chemical Thermodynamics," W. H. Freeman and Co., San Francisco, **1958**, p. 233.

which is involved here, it is only necessary to show that

$$\frac{d}{dx}(x \ln x - x + c) = \ln x$$

which is quite straightforward.

If, instead, one of the author's other two approaches, involving the proof of

$$1 + 1/2 + 1/3 + \ldots + 1/N_i \approx \ln N_i$$

is followed, then, when Stirling's approximation is needed later on in various applications of the Boltzmann distribution law, it may be derived as follows. From

$$d \ln N! = (1 + 1/2 + 1/3 + \ldots + 1/N)dN \approx \ln N \, dN$$

we obtain

$$\int d \ln N! \approx \int \ln N \, dN$$

whence

$$\ln N! = N \ln N - N + c$$

$$\approx N \ln N - N; \quad N \gg c$$