Thermodynamics and Statistical Mechanics Equilibrium by Entropy Maximization

Phil Attard

Corrections to the First Edition (2002), as at 11 Jan., 2010.

Pages 8–10, (and also Appendix A). The discussion of probability and set theory often implicitly used the same symbol to represent both a specific macrostate and the entire collective of such macrostates. The presentation would arguably be clarified by distinguishing these. For example, the label α should be taken to represent a specific macrostate, which comprises all microstates that have macroscopic value equal to α, belonging to the collective of similar macrostates, (e. g. $\alpha = 10$J, and it belongs to the energy collective). Macrostates in a given collective must be disjoint, (which means the weight $\omega(\alpha, \beta) = 0$ if $\alpha \neq \beta$ and α and β represent macrostates in the same collective), but macrostates belonging to different collectives may overlap, (e. g. $\omega(\alpha, \beta)$ may be non-zero if α is an energy state in the collective of energy macrostates and β is a volume state in the collective of volume macrostates).

Page 13, following Eq. (1.16): Replace the definition of the average by $\langle f \rangle = \int \mathrm{d}\mathbf{x}\, \omega(\mathbf{x}) f(\mathbf{x})/W$.

Page 72, Eq. (4.58): Replace the right hand side argument $(E|N, V, T)$ by $(E, N|\mu, V, T)$.

Page 77. Replace Eqs (4.91–94) and surrounding text by:

One can also define the usual heat capacity, (c. f. Eq. (3.63)),

$$C_{\mathrm{p}} \equiv \left(\frac{\partial \overline{H}(N, p, T)}{\partial T} \right)_{N,p} = \frac{-\beta}{T} \frac{\partial^2 \beta \overline{G}(N, p, T)}{\partial \beta^2}, \tag{4.91}$$

and in the thermodynamic limit one has

$$\left\langle \Delta(H)^2 \right\rangle = \frac{T}{\beta} C_{\mathrm{p}}, \tag{4.92}$$

which shows that C_{p} is positive. Note that an alternative heat capacity at constant pressure is related to the usual heat capacity just defined by

$$\begin{aligned} \tilde{C}_{\mathrm{p}} \equiv \left(\frac{\partial \overline{E}(N, p, T)}{\partial T} \right)_{N,p} &= \frac{-\beta}{T} \frac{\partial^2 \beta \overline{G}(N, p, T)}{\partial \beta^2} - p \frac{\partial^2 \overline{G}(N, p, T)}{\partial T \partial p} \\ &= C_{\mathrm{p}} - \alpha p \overline{V}(N, p, T), \end{aligned} \tag{4.93}$$

where the coefficient of thermal expansion is

$$\alpha \equiv \frac{1}{\overline{V}(N,p,T)} \left(\frac{\partial \overline{V}(N,p,T)}{\partial T} \right)_{N,p}. \tag{4.94}$$

Page 96, fourth line after Eq. (5.41): Replace 'and' by 'an'.

Page 119, Top of page should read $T \to 0$.

Page 119. Following Eq. (6.28) the low temperature limit should read $C_{\mathrm{V}} \to M k_{\mathrm{B}} \ln^2(N/M)$, $M \ll N$.

Page 119, Eqs (6.29) and (6.30). Replace $N/2$ in the exponent by $3N/2$, (three occurrences).

Page 130, Eq. (6.73) should read

$$u_{in} = \sqrt{\frac{2}{N}} \sin \frac{in\pi}{N+1}, \ 1 \le i \le N, \ 1 \le n \le N, \ N > 1. \tag{6.73}$$

Page 133, immediately following Eq. (6.88). Replace 'incompressible' by 'infinitely compressible'.

Page 169. Replace Eq. (7.58) and associated text by:

One possible choice is $\mathbf{n}(\mathbf{\Gamma}) = \sum_{i\alpha} p_{i\alpha} \hat{\mathbf{p}}_{i\alpha}$, in which case

$$\nabla \cdot \tilde{\mathbf{n}}(\mathbf{\Gamma}) = \frac{3N/2}{\sum_{i\alpha} p_{i\alpha}^2/2m} + \dots, \tag{7.58}$$

where terms not shown may be neglected in the thermodynamic limit. The average of this in that same limit is $\langle \nabla \cdot \tilde{\mathbf{n}} \rangle = 1/k_{\mathrm{B}}T$.

Page 178, Eq. (7.93): Insert a factor of β before the integral sign.

Page 231, Eq. (9.92): On the right hand side of the first equality, move the volume V from the denominator to the numerator.

Page 244, Eq. (10.2): The right hand side of the second equality should read $\tilde{E} - \mu \tilde{N} - TS(\tilde{E}, \tilde{N}, V)$.

Page 325, fifth line: Replace 'is faster than' by 'decays like'.

Page 365, following Eq. (13.30): The pseudo-chemical potential should read $\tilde{\mu} = \mu - 3k_{\mathrm{B}}T \ln \Lambda$.