Helmholtz Free Energy in terms of the (canonical) partition function

We want to prove that:

$$A(N,V,\beta) = -k_B T \cdot \ln[Q(N,V,\beta)] \quad (I)$$

$$A = E - TS \quad (II)$$

$$\frac{\partial A}{\partial T} = -S \Rightarrow S = -\frac{\partial A}{\partial T} \quad (III)$$

$$E = \langle H(x) \rangle = \frac{\int H(x) \cdot e^{-\beta H(x)} dx}{\int e^{-\beta H(x)} dx}$$

$$= \frac{\int H(x) \cdot e^{-\beta H(x)} dx}{Q(N,V,\beta)}$$

$$= \frac{1}{Q(N,V,\beta)} \cdot -\frac{\partial}{\partial \beta} Q(N,V,\beta)$$

$$= -\frac{\partial}{\partial \beta} \ln Q(N,V,\beta) \quad (IV)$$

We substitute (III) and (IV) in (II):

$$A = -\frac{\partial}{\partial \beta} \ln Q(N,V,\beta) + T \cdot \frac{\partial A}{\partial T}$$

Note that:

$$T \cdot \frac{\partial A}{\partial T} = T \cdot \frac{\partial A}{\partial \beta}\frac{\partial \beta}{\partial T} = -T \cdot \frac{\partial A}{\partial \beta} \cdot \frac{1}{k_B T^2} = -\beta \frac{\partial A}{\partial \beta}$$

So that we get:

$$A + \frac{\partial}{\partial \beta} \ln Q(N,V,\beta) + \beta \frac{\partial A}{\partial \beta} = 0 \quad (V)$$

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Now we have to prove that (I) is indeed a solution of (V)...

$$\frac{\partial A}{\partial \beta} = \frac{\partial}{\partial \beta}\left[-k_B T \cdot \ln Q(N,V,\beta)\right]$$

$$\Rightarrow -\frac{\partial A}{\partial \beta} = \frac{\partial}{\partial \beta}\left[\frac{1}{\beta} \cdot \ln Q(N,V,\beta)\right]$$

$$= -\frac{1}{\beta^2} \cdot \ln Q(N,V,\beta) + \frac{1}{\beta} \cdot \frac{\partial}{\partial \beta} \ln Q(N,V,\beta)$$

$$= -\frac{1}{\beta} \cdot \left[\frac{1}{\beta} \cdot \ln Q(N,V,\beta) - \frac{\partial}{\partial \beta} \ln Q(N,V,\beta)\right]$$

$$\Rightarrow \beta \frac{\partial A}{\partial \beta} = \frac{1}{\beta} \cdot \ln Q(N,V,\beta) - \frac{\partial}{\partial \beta} \ln Q(N,V,\beta) \quad (VI)$$

If we substitute (I) and (VI) into (V)...

$$-\frac{1}{\beta} \cdot \ln Q(N,V,\beta) + \frac{\partial}{\partial \beta} \ln Q(N,V,\beta) + \frac{1}{\beta} \cdot \ln Q(N,V,\beta) - \frac{\partial}{\partial \beta} \ln Q(N,V,\beta) = 0$$

$$0 = 0$$

Wheighted Histogram Analysis Method
The weights (partial derivation)

$$\mathcal{L}(m_i,\lambda) = \sigma^2[P_u] - \lambda(\sum_i m_i - 1)$$

$$= \sum_i m_i^2 \sigma^2[P_u^i] - \lambda(\sum_i m_i - 1)$$

$$\frac{\partial \mathcal{L}(m_i,\lambda)}{\partial m_i} = 0$$

$$2m_i\sigma^2[P_u^i] - \lambda = 0$$

$$m_i = \frac{\lambda}{2\sigma^2[P_u^i]} \quad (1)$$

$$\frac{\partial \mathcal{L}(m_i,\lambda)}{\partial \lambda} = 0$$

$$\sum_i m_i = 1 \quad (2)$$

$$(1) \rightarrow (2) \Rightarrow \sum_j \frac{\lambda}{2\sigma^2[P_u^j]} = 1$$

$$\lambda = 2\sum_j \sigma^2[P_u^j] \quad (3)$$

$$(3) \rightarrow (1) \Rightarrow m_i = \frac{\sum_j \sigma^2[P_u^j]}{\sigma^2[P_u^i]}$$

$$P_{unbiased}(s) \propto \sum_{i=1}^{N_{MD}} \frac{\sum_{j=1}^{N_{MD}} \sigma^2[P_{unbiased}(s^{*(j)})]}{\sigma^2[P_{unbiased}(s^{*(i)})]} \cdot P_{unbiased}(s^{*(i)})$$