



**MathsNET**

A joined up approach to  
teaching and learning  
mathematics

# The canonical ensemble

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- What thermodynamic potential can be calculated from the canonical partition function? How is this done and how is this result derived?
- Give an expression that allows one to calculate the ensemble average,  $\langle A \rangle$ , for the observable  $A$ . You may assume that this quantity can be calculated based on the positions,  $\mathbf{x}$ , and momenta,  $\mathbf{p}$ , of the atoms using a function  $A(\mathbf{x}, \mathbf{p})$ .
- Explain why  $1 = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j) - \Psi}$
- Now calculate the first derivative of  $1 = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j) - \Psi}$  with respect to  $\beta$  and hence show that  $\langle E \rangle = -\frac{\partial \Psi}{\partial \beta}$



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- Calculate the second derivative of  $1 = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j) - \Psi}$  with respect to  $\beta$  and hence show that  $\langle (H - \langle E \rangle)^2 \rangle = \frac{\partial^2 \Psi}{\partial \beta^2}$
- Explain (in your own words) why  $\langle (H - \langle E \rangle)^2 \rangle = -\frac{\partial \langle E \rangle}{\partial \beta}$ .
- Use the chain rule to show that:  $\frac{\partial \langle E \rangle}{\partial \beta} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}$
- Use the result you have just arrived at to write an expression that tells you how the heat capacity can be calculated from the fluctuations in the total energy  $\langle (H - \langle E \rangle)^2 \rangle$