Thermodynamics of materials

15. Two state paramagnet and partition function for rotational energy states

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Two state paramagnet

- Assume the two state paramagnet, assume two possible energies, $-\mu B$ and $+\mu B$,

$$Z = \sum_s e^{\frac{-E_s}{k_\mathsf{B} T}} = e^{\frac{\mu B}{k_\mathsf{B} T}} + e^{\frac{-\mu B}{k_\mathsf{B} T}} = 2\cosh\left(\frac{\mu B}{k_\mathsf{B} T}\right)$$

- The probabilities would then be

$$P_\uparrow = \frac{e^{\frac{\mu B}{k_\mathsf{B} T}}}{2\cosh\left(\frac{\mu B}{k_\mathsf{B} T}\right)} \qquad P_\downarrow = \frac{e^{\frac{-\mu B}{k_\mathsf{B} T}}}{2\cosh\left(\frac{\mu B}{k_\mathsf{B} T}\right)}$$

Two state paramagnet

- The average energy of a molecule would be

$$\overline{E} = \frac{1}{Z}\sum_s E(s)e^{-\beta E_s} = -\mu B P_\uparrow + \mu B P_\downarrow = -\mu B \frac{e^{\frac{\mu B}{k_\mathrm{B} T}} - e^{\frac{-\mu B}{k_\mathrm{B} T}}}{2\cosh\left(\frac{\mu B}{k_\mathrm{B} T}\right)}$$

$$= -\mu B \frac{2\sinh\left(\frac{\mu B}{k_\mathrm{B} T}\right)}{2\cosh\left(\frac{\mu B}{k_\mathrm{B} T}\right)} = -\mu B \tanh\left(\frac{\mu B}{k_\mathrm{B} T}\right)$$

- For the collection of N, the internal energy would be

$$U = -N\mu B \tanh\left(\frac{\mu B}{k_\mathrm{B} T}\right)$$

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Rotational Kinetic Energy of Molecules

- In Quantum mechanics, angular momentum of quantum system is

$$E_{\text{rot}} = E_J = \frac{\hbar^2}{2I} J(J+1) = \varepsilon J(J+1) \qquad J = 0, 1, 2, \cdots$$

where J is the orbital quantum number and considering orbital magnetic quantum number, the degeneracy of state at J orbital quantum number is $2J+1$.

- At classical mechanics limit, $dJ \to 0$, in other words, $k_{\text{B}}T \gg \varepsilon$, the partition function is given by

$$Z = \sum_{s=1}^{\infty} \exp\left(-\frac{E_s}{k_{\text{B}}T}\right) = \sum_{J+1}^{\infty} (2J+1) \exp\left(\frac{-\varepsilon J(J+1)}{k_{\text{B}}T}\right)$$
$$\simeq \int_0^{\infty} (2J+1) \exp\left(\frac{-\varepsilon J(J+1)}{k_{\text{B}}T}\right) dJ = \frac{k_{\text{B}}T}{\varepsilon}$$

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Average energy of the system at given temperature

- The average energy of the system at given T is

$$\overline{E} = \frac{\sum E_s \exp\big(-\beta E_s\big)}{\sum \exp\big(-\beta E_s\big)} = \frac{\sum E_s \exp\big(-\beta E_s\big)}{Z}$$

- Since we have

$$\frac{\partial Z}{\partial \beta} = \sum -E_s \exp\big(-\beta E_s\big)$$

therefore,

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

Average energy of the system at given temperature

- At high temperature, $k_{\mathrm{B}}T \gg \varepsilon$,

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\varepsilon}{k_{\mathrm{B}}T}\frac{\partial}{\partial \beta}\frac{k_{\mathrm{B}}T}{\varepsilon} = -\varepsilon\beta\frac{\partial}{\partial \beta}\left(\frac{1}{\beta\varepsilon}\right) = \frac{1}{\beta} = k_{\mathrm{B}}T$$

which yields the average rotational energy.