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Course 565/665 Lecture Number ____ Date 3/28/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Last Time

Factoring Q: How do you define the partition function "q" of subsystems of a system whose overall partition function is Q.

- N Independent Distinguishable Particles

a) All particles have the same q.

$$Q = \prod_{i=1}^{N} q_i = q^N$$

b) Particles have different q's.

$$Q = \prod_{i=1}^{N} q_i = q_1 \cdot q_2 \cdot q_3 \cdot \cdots \cdot q_N$$

- N Independent Indistinguishable Particles

a) $Q = \dfrac{q^N}{N!}$

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Predicting Thermodynamic Functions, T, V, N constant

U

$$U = \langle E \rangle = \sum_{i=1}^{N} p_i(T)\, E_i(V,N)$$

- $E_i(V,N)$ is the ~~average~~ energy of a particular molecule.
- In addition, this is a postulate of Gibbs Thermodynamics.

$$\langle E \rangle = \sum_{i=1}^{N} p_i(T)\, E_i(V,N) = \frac{\sum_{i=1}^{N} e^{-\beta E_i} \cdot E_i}{Q}$$

where $\beta = \frac{1}{kT}$

$$\left(\frac{\partial Q}{\partial \beta}\right)_{N,V} = \frac{\partial}{\partial \beta}\left(\sum_{j=1}^{N} e^{-\beta E_j}\right) = -\sum_{j=1}^{N} E_j\, e^{-\beta E_j}$$

$$U = \langle E \rangle = \frac{-1}{Q} \cdot \left(\frac{\partial Q}{\partial \beta}\right) = \frac{1}{Q} \sum_{j=1}^{N} E_j\, e^{-\beta E_j}$$

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Thus,

$$\langle E \rangle = U = \frac{-1}{Q}\left(\frac{\partial Q}{\partial \beta}\right) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

Also,

$$\frac{\partial}{\partial \beta} = \frac{\partial}{\partial T}\left(\frac{\partial T}{\partial \beta}\right) \quad \text{OR} \quad \frac{\partial}{\partial T} = \frac{\partial}{\partial \beta}\left(\frac{\partial \beta}{\partial T}\right)$$

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

$$\frac{\partial}{\partial \beta} = -kT^2 \frac{\partial}{\partial T}$$

Finally,

$$\boxed{\langle E \rangle = U = -\frac{\partial \ln Q}{\partial \beta} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}}$$

$$\langle E \rangle \longrightarrow \langle \varepsilon \rangle$$

$$\langle \varepsilon \rangle = \frac{kT^2}{N}\left(\frac{\partial \ln q^N}{\partial T}\right) = kT^2\left(\frac{\partial \ln q}{\partial T}\right)$$

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$\boxed{S}$ $$\frac{S}{k} = -\sum_{j=1}^{N} p_i \ln p_i \qquad \text{where} \quad p_i = \frac{e^{-\beta E_i}}{Q}$$

$$\frac{S}{k} = -\sum_{j=1}^{N} \left(\frac{1}{Q} \cdot e^{-\beta E_i}\right)\left(\frac{-E_i}{kT} + \ln\left(\frac{1}{Q}\right)\right)$$

$$S = kN \ln q + \frac{U}{T}$$

<u>Table</u>

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)$$

$$S = k \ln Q + \frac{U}{T}$$

$$F = U - TS = -kT \ln Q$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = +kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

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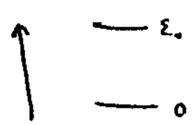
The 2-state System/Model (Example 10.5)

Scholtky Model:

$\langle \varepsilon \rangle$, C_v, $\frac{S}{N}$?



$$q = \sum_{i=1}^{2} e^{-\beta \varepsilon_i}$$

$$q = e^{-0} + e^{-\beta \varepsilon_0}$$

$$\boxed{q = 1 + e^{-\beta \varepsilon_0}}$$