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Course 565/665 Lecture Number ______ Date 3/24/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Test Results

Average: 81

Approximate Cutoffs

88+	A, AB
88-72	B
72-65	BC, C
65-	D

Within the next 10 days, you need to choose a topic for the end of the class presentation.

The Boltzmann Distribution Function

- Dealing with systems where each particle has a given energy.

Consider: N noninteracting particles.

E_J with $J = 1, 2, \ldots t$

i.e. we have "t" energy levels.

- We know the values for E_j
- E_j values are defined by the nature of the problem or by experience.

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- Operate @ T, V, N constant.

Recall:
$$\frac{S}{Nk} = -\sum_{j=1}^{t} p_j \ln p_j$$
$$dS = -Nk \sum_{j=1}^{t} (1 + \ln p_j)\, dp_j$$

Postulate:
$$U = \langle E \rangle = \sum_{j=1}^{t} p_j E_j$$

$$dU = d\langle E \rangle = \sum_{j=1}^{t} (E_j\, dp_j + p_j\, dE_j)$$

NOTE: ① $U(S, N, V)$
② $E_j(N, V)$ [Independent of S]

The energy levels themselves are not affected by S or T. They are defined by quantum mechanics. The populations of the states are defined by the temperature.

③ $p_j = p_j(T)$ and $E_j \neq E_j(T)$

Then. ④ $\langle E \rangle = \sum_{j=1}^{t} p_j(T)\, E_j \Rightarrow \langle E \rangle = \langle E(T) \rangle$

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$$dE_j = \left(\frac{\partial E_j}{\partial V}\right)_N dV + \left(\frac{\partial E_j}{\partial N}\right)_V dN = 0$$

$$dU = d\langle E\rangle = \sum_{j=1}^{t} E_j \, dp_j$$

From 1st Law:

$$dU = \delta q + \delta w = \delta q \quad \text{(at constant } N, V)$$

$$d\langle E\rangle = dU = \sum_{j=1}^{t} E_j \, dp_j = \delta q$$

Also: $$\sum_{j=1}^{t} p_j \, dE_j = \delta w$$

Apply the eq. condition to F:

$$dF = dU - TdS - \cancel{SdT}^{\,0} = d\langle E\rangle - TdS = 0$$

$$dF = d\langle E\rangle - TdS$$

Also, $$\sum_{j=1}^{t} p_j = 1$$

$$d\sum_{j=1}^{t} dp_j = 0$$

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$$dF = d\langle E \rangle - T\,dS$$

$$= \sum_{j=1}^{t} \left(E_j + kNT\left(1 + \ln p_j^*\right) + \alpha \right) dp_j^* = 0$$

$$\ln p_j^* = \frac{-E_j}{NkT} - \frac{\alpha}{NkT} - 1$$

$$p_j^* = e^{-E_j/NkT}\, e^{[(-\alpha/NkT)-1]}$$

$$\sum_{j=1}^{t} p_j = 1 \qquad \Big\} \quad \sum_{j=1}^{t} p_j^* = \sum_{j=1}^{t} e^{-E_j/NkT}\, e^{[(-\alpha/NkT)-1]} = 1$$

$$p_j^* = \frac{e^{-E_j/NkT}}{\sum_{j=1}^{t} e^{-E_j/NkT}}$$

Boltzmann Distribution: $$p_j^* = \frac{e^{-\varepsilon_j/kT}}{\sum_{j=1}^{t} e^{-\varepsilon_j/kT}} = \frac{e^{-\varepsilon_j/kT}}{Q}$$

E_j is for the system, ε_j is for the particle.