Thermodynamics of Materials

10th Lecture

2008. 4. 2 (Wed.)

Derivation of Boltzman Distribution

The most probable distribution of molecules on various accessible energy levels

Macrostate with the maximum number of microstates

→ Equilibrium

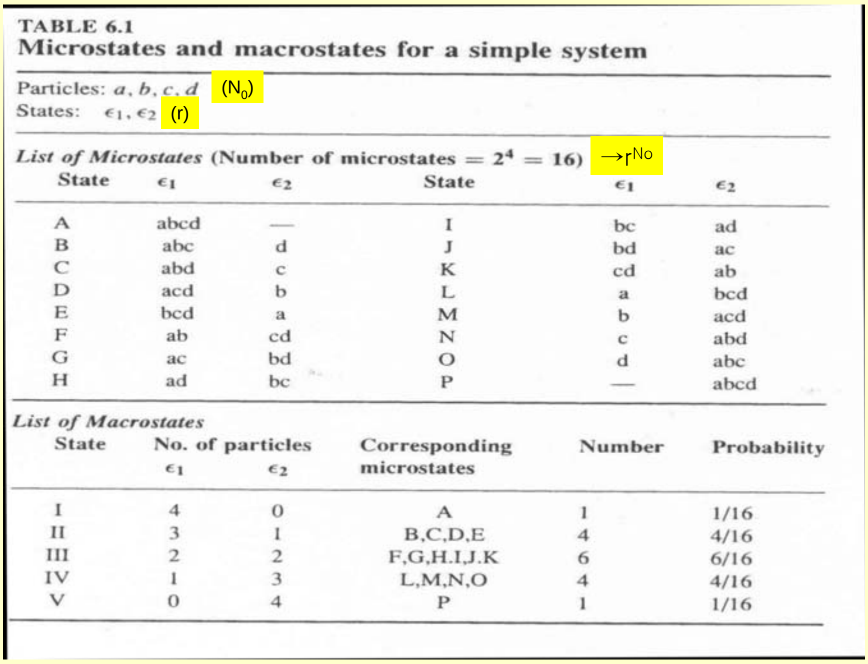

TABLE 6.1

Microstates and macrostates for a simple system

Particles: a, b, c, d (N_o)

States: ϵ_1, ϵ_2 (r)

List of Microstates (Number of microstates $= 2^4 = 16$) $\rightarrow r^{No}$

State	ϵ_1	ϵ_2	State	ϵ_1	ϵ_2
A	abcd	—	I	bc	ad
B	abc	d	J	bd	ac
C	abd	c	K	cd	ab
D	acd	b	L	a	bcd
E	bcd	a	M	b	acd
F	ab	cd	N	c	abd
G	ac	bd	O	d	abc
H	ad	bc	P	—	abcd

List of Macrostates

State	No. of particles ϵ_1	No. of particles ϵ_2	Corresponding microstates	Number	Probability
I	4	0	A	1	1/16
II	3	1	B,C,D,E	4	4/16
III	2	2	F,G,H,I,J,K	6	6/16
IV	1	3	L,M,N,O	4	4/16
V	0	4	P	1	1/16

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20 particle system with 7 energy states (1, 3, 4, 6, 2, 3, 1)

→20 particles are distributed among 7 accessible energy states.

→ 7 accessible energy states are partitioned among particles.

$$\Omega = \frac{20!}{1!3!4!6!2!3!1!}$$

macrostate (n_1, n_2, n_3, …, n_i, …, n_r) = (n_j)

→ distribution function

$$\Omega = \frac{N_o!}{n_1!n_2!\ldots n_r!}$$

$\Omega =$ number of microstates per macrostate
= total number of ways of arraning particles
to produce the distribution (n_j)

No. of microstates : $\Omega = \dfrac{N_o!}{n_1!n_2!\ldots n_r!}$

$$\boxed{S = k\ln\Omega}$$

The probability that the system exists in a given macrostate
$\rightarrow$ *the fraction of the time that it spends in microstates that correspond to that macrostate*
$\rightarrow$ *the ratio of the number of microstates Ω_J that correspond to the Jth macrostate to the total number of microstates the system may exhibit*

$$P_J = \frac{\Omega_J}{r^{N_0}} = \frac{N_0!}{\prod_{i=1}^{r} n_i!} \cdot \frac{1}{r^{N_0}}$$

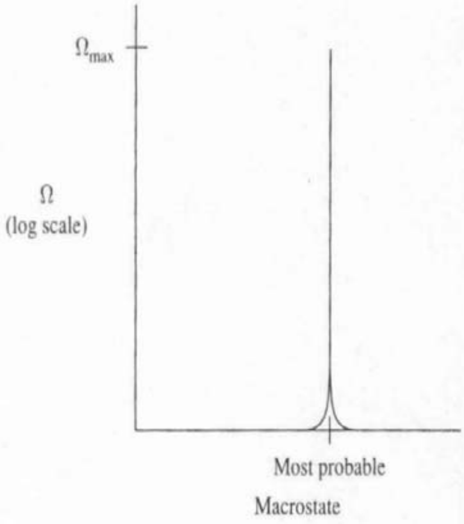

FIGURE 6.1
The probability distribution for macrostates has an extremely sharp peak for systems with large numbers of particles and macrostates.

How can we determine the macrostate with a maximum number of microstates?

$$\Omega = \left(\frac{N_0!}{\prod_{i=1}^{r} n_i!} \right)$$를 최대로 하는 macrostate, n_i

Ω는 너무 큰 숫자 이므로 다루기가 힘들다.
∴ logarithm 값을 사용한다.

$S = k \ln \Omega$ 라고 하고, S를 최대로 하는 macrostate, n_i, 를 구하면 된다.

$$S = k\ln\Omega = k\ln\left(\frac{N_0\,!}{\prod_{i=1}^{r} n_i\,!}\right)$$

$\ln x! \cong x\ln x - x$ → Stirling's approximation

$$S = -k\sum_{i=1}^{r} n_i \ln\left(\frac{n_i}{N_0}\right)$$

See the text for derivation.

S를 최대로 하는 조건 ? → dS = 0

$$dS = -k\sum_{i=1}^{r} \ln\left(\frac{n_i}{N_0}\right) dn_i$$

See the text for derivation.

Next step?

여기에 ***constraints****가 있다.*
이 ***constraints****를 만족시키면서 최대가 되는* ***S***

Which constraints ?

Isolated System
→ no transfer of energy and material

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$$U = \sum_{i=1}^{r} \varepsilon_i \cdot n_i = const. \quad N_0 = \sum_{i=1}^{r} n_i = const.$$

How do we use these constraints to derive the condition of maximum S ?

Constraints가 있을 때 maximize하는 방법
→ Method of Lagrange Multiplier

1. Multiply each of the differential forms of the constraining equations by an arbitrary constant.
2. Add these forms to the differential of the function whose extreme value is sought.
3. Set the coefficients of each of the differentials that appear in this equation equal to zero.
4. Solve the resulting set of equations, evaluating the Lagrange multipliers in the process.

$$dS = -k\sum_{i=1}^{r} ln\left(\frac{n_i}{N_0}\right)\cdot dn_i$$

$$U = \sum_{i=1}^{r}\varepsilon_i \cdot n_i = const. \rightarrow \qquad dU = \sum_{i=1}^{r}\varepsilon_i \cdot dn_i = 0$$

$$N_0 = \sum_{i=1}^{r} n_i = const. \rightarrow \qquad dN_0 = \sum_{i=1}^{r} dn_i = 0$$

$$\alpha\cdot dN_o = \alpha\sum_{i} dn_i = 0 \qquad \beta\cdot dU = \beta\cdot\sum_{i}\varepsilon_i dn_i = 0$$

$$dS + \alpha\cdot dN_0 + \beta\cdot dU = 0$$

substitute for dS, dN_0, and dU

$$-k\sum_{i=1}^{r} ln\left(\frac{n_i}{N_0}\right)\cdot dn_i + \alpha\cdot\sum_{i=1}^{r} dn_i + \beta\cdot\sum_{i}\varepsilon_i dn_i = 0$$

$$\sum_{i=1}^{r}\left[-k\,ln\left(\frac{n_i}{N_0}\right)+\alpha+\beta\varepsilon_i\right]dn_i = 0 \qquad -k\,ln\left(\frac{n_i}{N_0}\right)+\alpha+\beta\varepsilon_i = 0$$

$$\frac{n_i}{N_0} = e^{\alpha/k}\cdot e^{\beta\varepsilon_i/k}$$

$$\frac{n_i}{N_0} = e^{\alpha / k} \cdot e^{\beta \varepsilon_i / k}$$

n_i : *macrostate with a maximum number of microstates*

→ *Equilibrium*

→ *Boltzman distribution*

All we have to do is to determine α *and* β.

→ *How?*

$$\sum_{i=1}^{r} \frac{n_i}{N_0} = 1 = \sum_{i=1}^{r} e^{\alpha / k} \cdot e^{\beta \varepsilon_i / k} = e^{\alpha / k} \cdot \sum_{i=1}^{r} e^{\beta \varepsilon_i / k}$$

$$e^{\alpha / k} = \frac{1}{\sum_{i=1}^{r} e^{\beta \varepsilon_i / k}} = \frac{1}{P}$$

Partition function : $P = \sum_{i=1}^{r} e^{\beta \varepsilon_i / k}$

$$\frac{n_i}{N_0} = \frac{1}{P} e^{\beta \varepsilon_i / k}$$

$$\frac{n_i}{N_0} = \frac{1}{P} e^{\beta\varepsilon_i / k}$$

$$dS = -k \sum_{i=1}^{r} ln\left(\frac{n_i}{N_0}\right) \cdot dn_i$$

$$dS = -k \sum_{i=1}^{r} ln\left(\frac{1}{P} \cdot e^{\beta\varepsilon_i / k}\right) \cdot dn_i$$

$$dS = -k \sum_{i=1}^{r} \left(\frac{\beta\varepsilon_i}{k} - ln\,P\right) \cdot dn_i$$

$$dS = -\beta \sum_{i=1}^{r} \varepsilon_i dn_i + k\,ln\,P \cdot \sum_{i=1}^{r} dn_i$$

$$dS = -\beta dU + k\,ln\,P \cdot dN_0$$

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How can we determine β?

$$dU = TdS - P_{prs} dV + \mu dN_0$$

$$dS = \frac{1}{T} dU + \frac{P_{prs}}{T} dV - \frac{\mu}{T} dN_0$$

$$\beta = -\frac{1}{T}$$

$$\frac{\mu}{T} = k\,ln\,P \rightarrow \mu = kT\,ln\,P$$

$$\beta = -\frac{1}{T}$$

$$\frac{n_i}{N_0} = \frac{1}{P} e^{-(\varepsilon_i / kT)}$$

$$P \equiv \sum_{i=1}^{r} e^{-(\varepsilon_i / kT)}$$: *Partition function*

→ *Boltzman Distribution*

$$\frac{n_i}{N} = \frac{1}{P_{MB} e^{\varepsilon_i / kT}}$$

Boltzman Distribution

$$\frac{n_i}{N} = \frac{1}{P_{MB} e^{\varepsilon_i / kT}} = \frac{e^{-(\varepsilon_i / kT)}}{\sum_{i=1}^{r} e^{-(\varepsilon_i / kT)}}$$

$$P \equiv \sum_{i=1}^{r} e^{-(\varepsilon_i / kT)}$$: *Partition function*

Alternate Statistical Formulations

Maxwell-Boltzmann
Distribution: Boltzon :
distinguishable

$$\frac{n_i}{N} = \frac{1}{P_{MB}\, e^{\varepsilon_i / kT}}$$

Bose-Einstein Distribution
Boson : indistinguishable
and symmetric

$$\frac{n_i}{N} = \frac{1}{P_{BE}\left(e^{\varepsilon_i / kT} - 1\right)}$$

Fermi-Dirac Distribution
Fermion: indistinguishable and
anti-symmetric

$$\frac{n_i}{N} = \frac{1}{P_{FD}\left(e^{\varepsilon_i / kT} + 1\right)}$$

Calculation of the Macroscopic Properties from the Partition Function

$$P \equiv \sum_{i=1}^{r} e^{-(\varepsilon_i / kT)} \; : \quad \text{Partition function}$$

First, evaluate entropy.

$$S = -k\sum_{i=1}^{r} n_i \ln\left(\frac{n_i}{N_0}\right) \quad = -k\sum_{i=1}^{r} n_i \ln\left[\frac{1}{P} e^{-(\varepsilon_i / kT)}\right]$$

$$= -k\sum_{i=1}^{r} n_i \left[-\frac{\varepsilon_i}{kT} - \ln P\right] = +\frac{k}{kT}\sum_{i=1}^{r} \varepsilon_i n_i + k \ln P \sum_{i=1}^{r} n_i$$

$$S = \frac{1}{T} U + N_0 k \ln P$$

Calculation of the Macroscopic Properties from the Partition Function

$$S = \frac{1}{T}U + N_0 k \ln P$$

Using this equation, derive Helmholz free energy in terms of partition function P.

$$F \equiv U - TS = U - T\left[\frac{1}{T}U + N_0 k \ln P\right]$$

$$F = -N_0 kT \ln P$$

$$F = -N_0 kT \ln P$$

Using this equation, derive entropy not expressed by internal energy.

$$dF = -SdT - PdV + \delta W' \qquad S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$S = N_0 k \ln P + N_0 kT\left(\frac{\partial \ln P}{\partial T}\right)_V$$

$$F = -N_0 kT \ln P$$

$$S = N_0 k \ln P + N_0 kT \left(\frac{\partial \ln P}{\partial T}\right)_V$$

Using these two equations, derive internal energy in terms of partition function P.

$$U = F + TS = -N_0 kT \ln P + T\left[N_0 k \ln P + N_0 kT \left(\frac{\partial \ln P}{\partial T}\right)_V\right]$$

$$U = N_0 kT^2 \left(\frac{\partial \ln P}{\partial T}\right)_V$$

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Using this equation, derive heat capacity at constant volume.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 2N_0 kT \left(\frac{\partial \ln P}{\partial T}\right)_V + N_0 kT^2 \left(\frac{\partial^2 \ln P}{\partial T^2}\right)_V$$

Volume이 일정한 상태에서 구하므로 C_v를 구함
그러나 우리는 C_p를 알아야 함 →ΔH, ΔS

Once we obtain C_v, how do we obtain C_p ?

$$C_p - C_v = \alpha^2 VT / \beta$$

α and β are the coefficients of expansion and compressibility

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$V = V_o(1+\alpha\cdot\Delta T) \qquad \alpha = \frac{1}{\Delta T}\frac{\Delta V}{V_o}$$

$$C_p - C_v = \alpha^2 VT / \beta$$

Evaluate $C_p - C_v$ for ideal gas.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$PV = RT \qquad V = \frac{RT}{P} \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\cdot\frac{R}{P} = \frac{1}{T}$$

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{RT}{P^2}\right) = \frac{1}{P}$$

$$C_p - C_V = \frac{1}{T^2}VTP = R \qquad C_p - C_v = R$$

Atomistic Approach of Heat Capacity

- Einstein's Model of a Crystal
- Monatomic Gas Model

$$F = -N_0 kT \ln P$$

$$U = N_0 kT^2 \left(\frac{\partial \ln P}{\partial T} \right)_V$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 2N_0 kT \left(\frac{\partial \ln P}{\partial T} \right)_V + N_0 kT^2 \left(\frac{\partial^2 \ln P}{\partial T^2} \right)_V$$

Einstein's Model of a Crystal (only vibrational K.E.)

harmonic oscillator

$$\varepsilon_i = \left(i + \frac{1}{2} \right) \hbar \nu$$

Evaluate partition function.

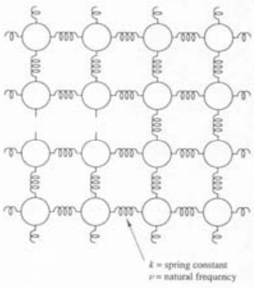

FIGURE 6.2
The Einstein model for a simple cubic crystal. Atoms vibrate about their equilibrium positions harmonically, as if joined by simple, ideal springs.