Ch. 9. Statistical Mechanics

Maxwell-Boltzmann Distribution

- Classical statistics: distinguishable particles

Bose-Einstein Distribution

- QM statistics: indistinguishable particles

  bosons (integer spin: 예 – photons)

Fermi-Dirac Distribution

- QM statistics: indistinguishable particles

  fermions (spin=1/2, 3/2,…: 예: electrons)

29
12
8
19
31
18
6
21
33

Based on …

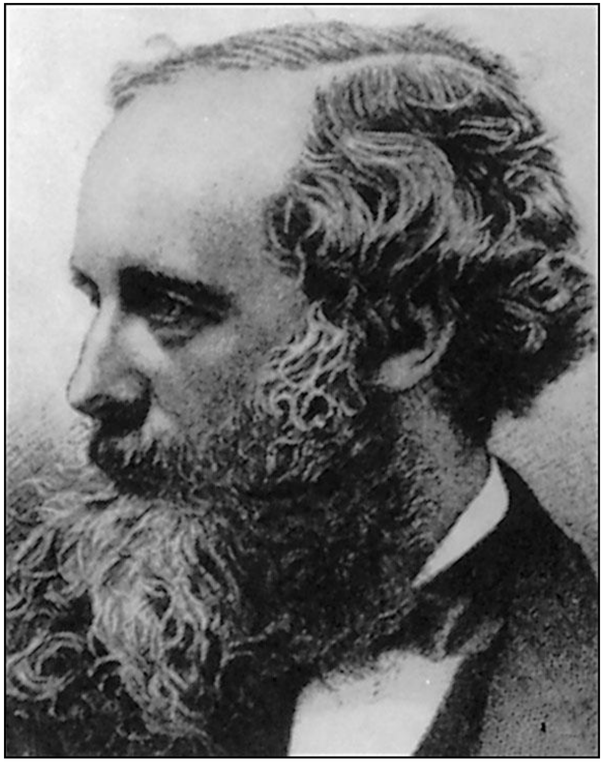
확률

경우의 수

Most probable configuration

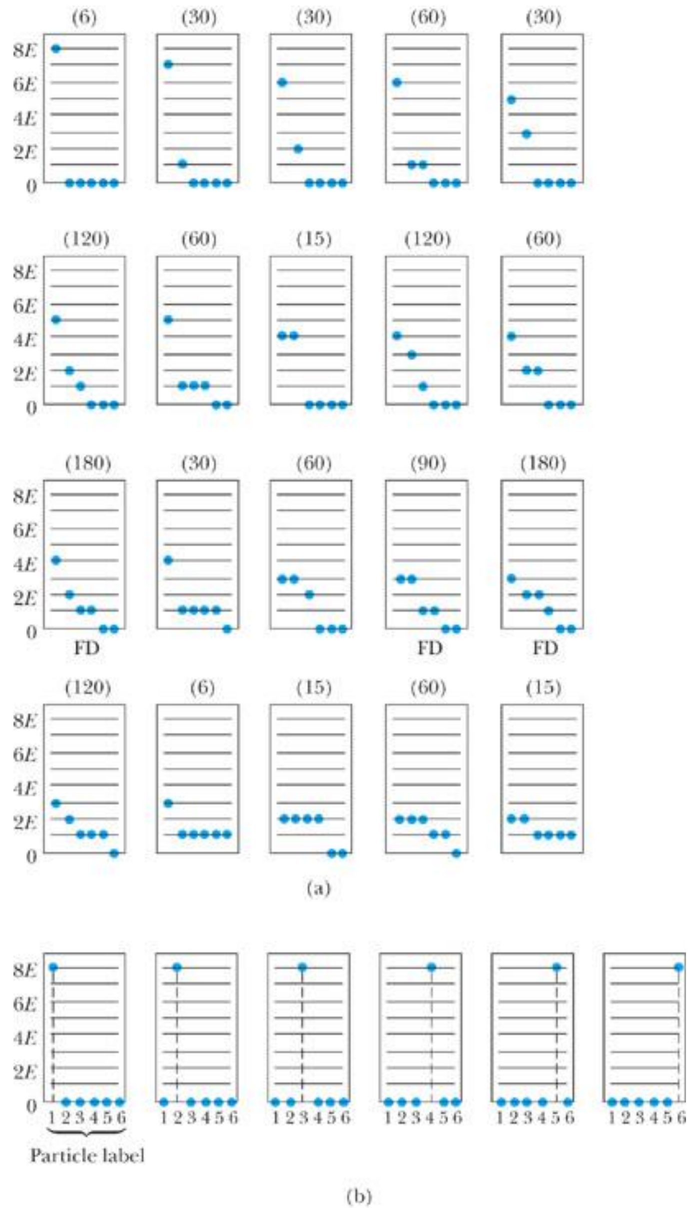
예: Random walk problem

Maxwell and Boltzmann



James Clerk Maxwell
(1831-1879)

Ludwig Boltzmann
(1844-1908)


(6) (30) (30) (60) (30)
(120) (60) (15) (120) (60)
(180) (30) (60) (90) (180)
FD FD FD
(120) (6) (15) (60) (15)
8E 6E 4E 2E 0
(a)
1 2 3 4 5 6
Particle label
(b)

Example

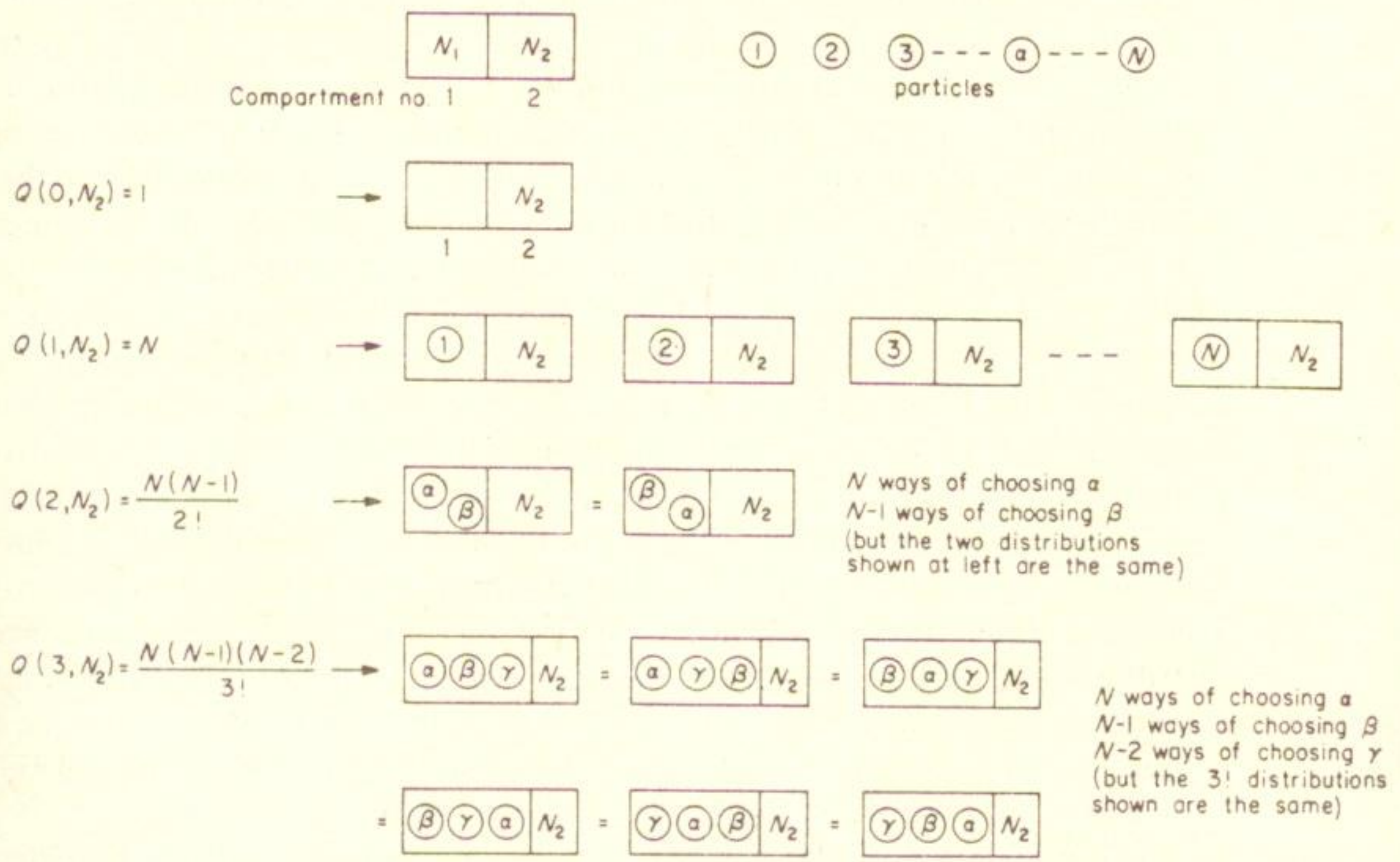


FIGURE 5.2. The possible ways of distributing N identifiable particles among two containers.

Most Probable Configuration

$$N = N_1 + N_2 + \cdots + N_n$$

$$U = E_1 N_1 + E_2 N_2 + \cdots + E_n N_n$$

$$Q(N_1, N_2, \cdots, N_n) = \frac{N!}{N_1! N_2! \cdots N_n!}$$

$$\ln Q(N_1, N_2, \cdots, N_n) \qquad \text{entropy}$$

Most Probable Configuration

Lagrange's multiplier method

$$\frac{\partial \ln Q}{\partial N_i} + \alpha \frac{\partial f}{\partial N_i} + \beta \frac{\partial h}{\partial N_i} = 0$$

Stirling's approximation

$$\ln(n!) \approx n \ln n - n \quad \text{for} \;\; n >> 1$$

$$-\frac{\partial \left(N_i \ln N_i - N_i \right)}{\partial N_i} + \alpha + \beta E_i = 0$$

$$N_i = e^{\alpha} e^{\beta E_i}$$

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

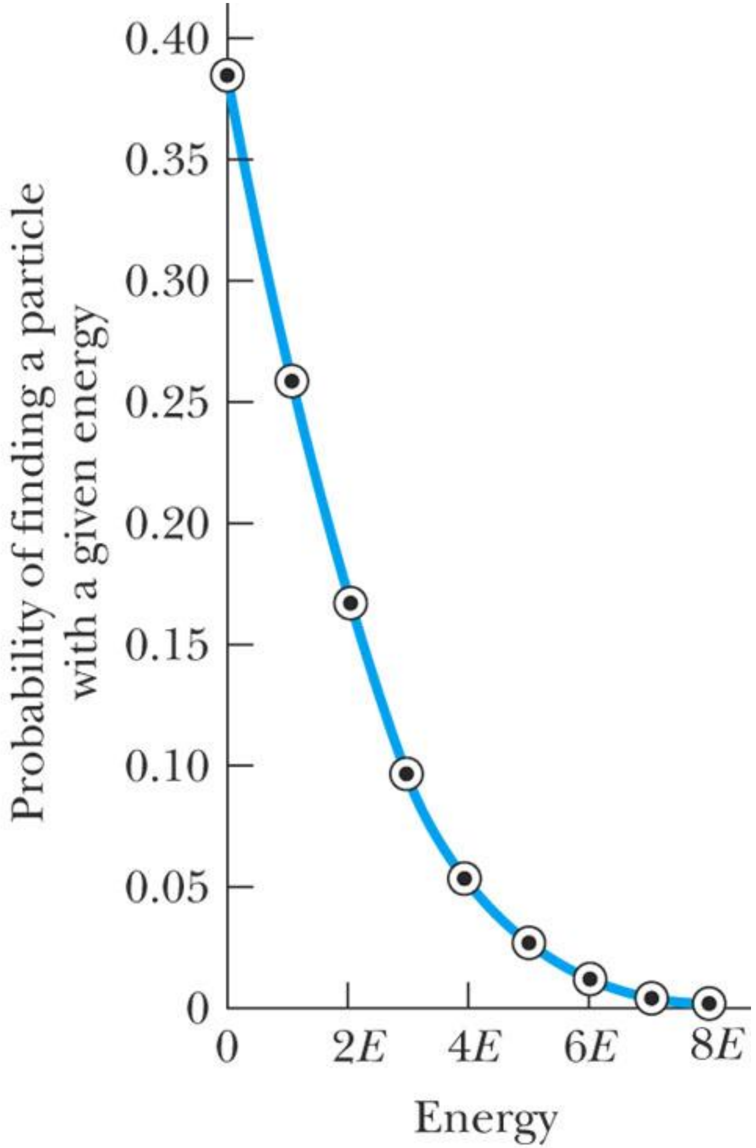
Maxwell-Boltzmann Distribution

$$f_{MB}(E_i) = A\exp\left(-\frac{E_i}{k_B T}\right)$$

$$n_i = g_i f_{MB} \rightarrow n(E)dE = g(E) f_{MB}(E)dE$$

$$N = \sum n_i \rightarrow \frac{N}{V} = \int_0^\infty n(E)dE = \int_0^\infty g(E) f_{MB}(E)dE$$

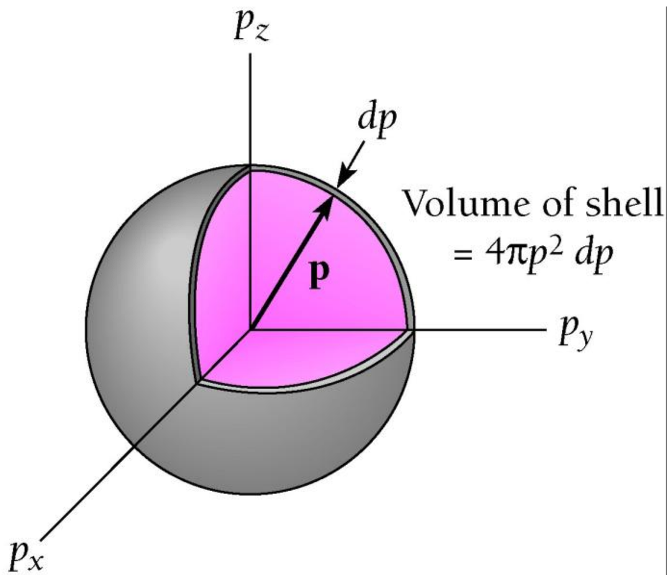
(경우에 따라서는 N/V 대신 N 사용)

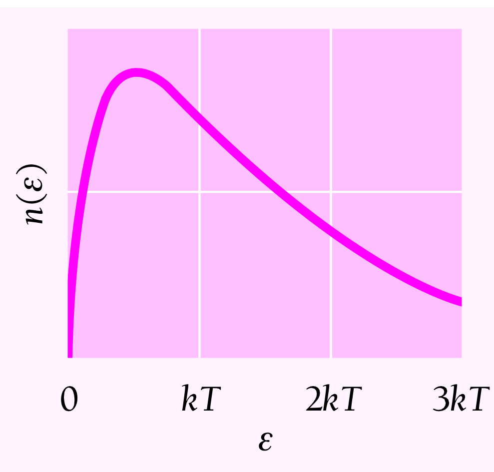


Probability of finding a particle with a given energy
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
0
2E
4E
6E
8E
Energy

Example

Ideal Gas





$$n(E)dE = \left[g(E)dE\right] f_{MB}(E) = Ag(E)\exp\left(-\frac{E}{k_B T}\right)dE$$

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$g(p)dp = Bp^2 dp$$

$$g(E)dE = g(p)dp = 2m^{3/2}B\sqrt{E}\,dE$$

$$n(E)dE = C\sqrt{E}\exp\left(-\frac{E}{k_B T}\right)dE$$

$$N = \int_0^\infty n(E)dE = C\int_0^\infty \sqrt{E}\exp\left(-\frac{E}{k_B T}\right)dE = \frac{C}{2}\sqrt{\pi}\left(k_B T\right)^{3/2}$$

$$n(E)dE = \frac{2\pi N}{\left(\pi k_B T\right)^{3/2}}\sqrt{E}\exp\left(-\frac{E}{k_B T}\right)dE$$

Ideal Gas

Total energy of *N* gas molecules

$$E = \int_0^\infty E n(E) dE = \frac{2\pi N}{(\pi k_B T)^{3/2}} \int_0^\infty E^{3/2} \exp\left(-\frac{E}{k_B T}\right) dE$$

$$= \frac{3}{2} N k_B T$$

Average molecular energy

$$\overline{E} = \frac{3}{2} k_B T$$

Equipartition of Energy

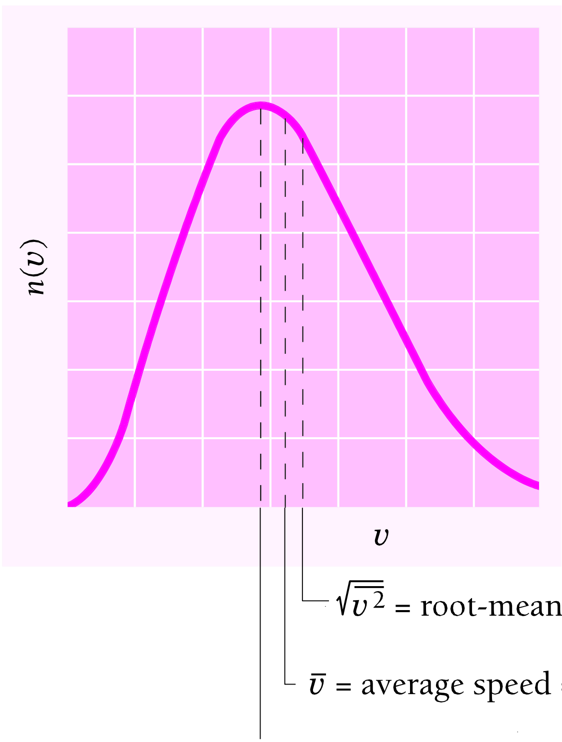
$$\frac{1}{2} m \left\langle v^2 \right\rangle = \bar{K} = \frac{3}{2} k_B T$$

$$\frac{1}{2} m \left\langle v_x^2 \right\rangle = \frac{1}{2} m \left\langle v_y^2 \right\rangle = \frac{1}{2} m \left\langle v_z^2 \right\rangle = \frac{1}{2} k_B T$$

A classical molecule in thermal equilibrium at temperature T has an average energy of $k_B T/2$ for each independent mode of motion or so-called degree of freedom.

Each variable that occurs squared in the formula for the energy of a particular system represents a degree of freedom subject to the equipartition of energy.

Maxwell's Speed Distribution



$$E = \frac{1}{2} m v^2$$

$$dE = m v dv$$

$$n(v) dv = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(-\frac{m v^2}{2 k_B T} \right) dv$$

$$v_{rms} = \sqrt{\left\langle v^2 \right\rangle} = \sqrt{\frac{3 k_B T}{m}}$$

Maxwell's Speed Distribution

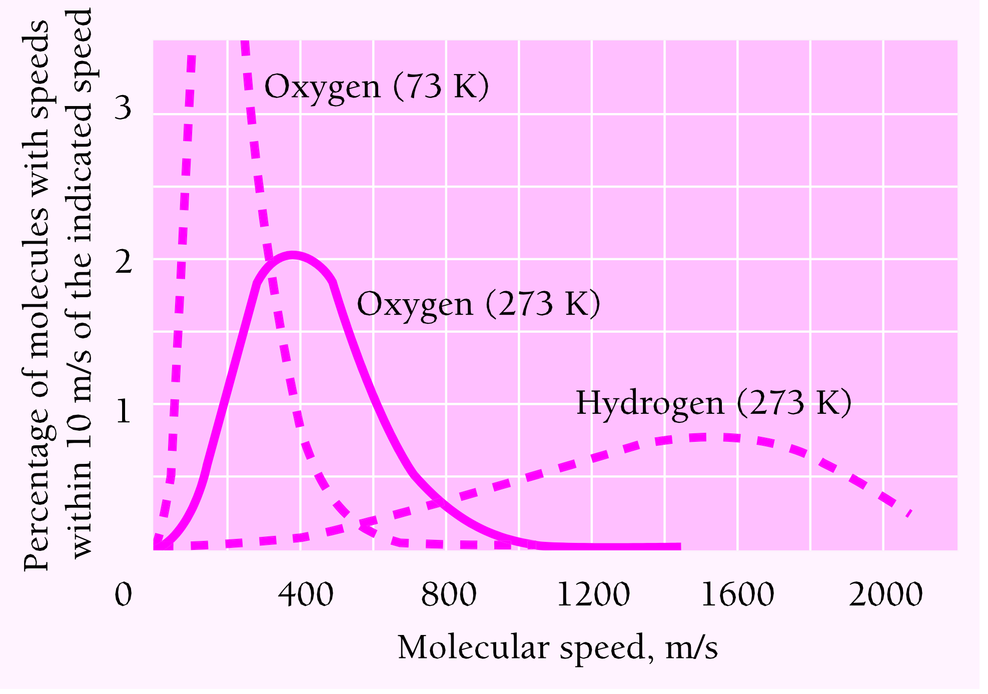


그림 9.4 73K의 산소, 273K의 산소, 그리고 273K의 수소에서의 분자 속력분포.