



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)



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Based on ...

확률

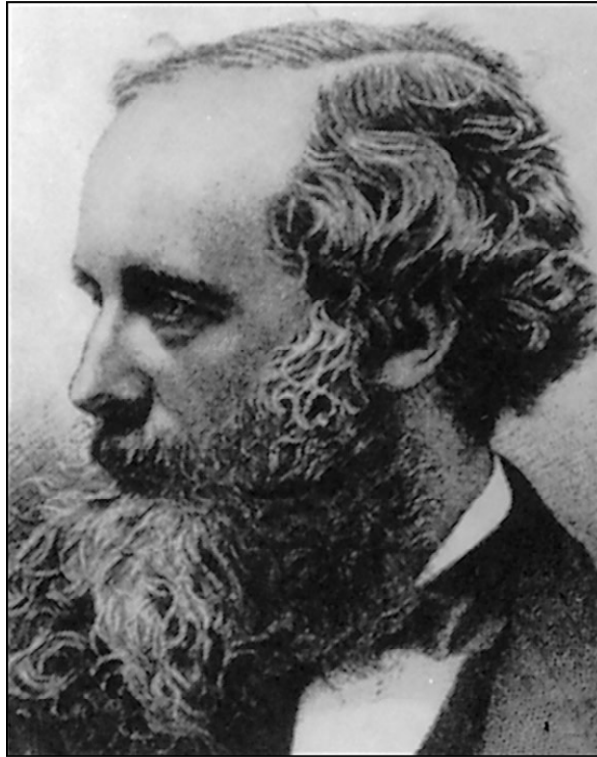
경우의 수

Most probable configuration

예: Random walk problem



Maxwell and Boltzmann



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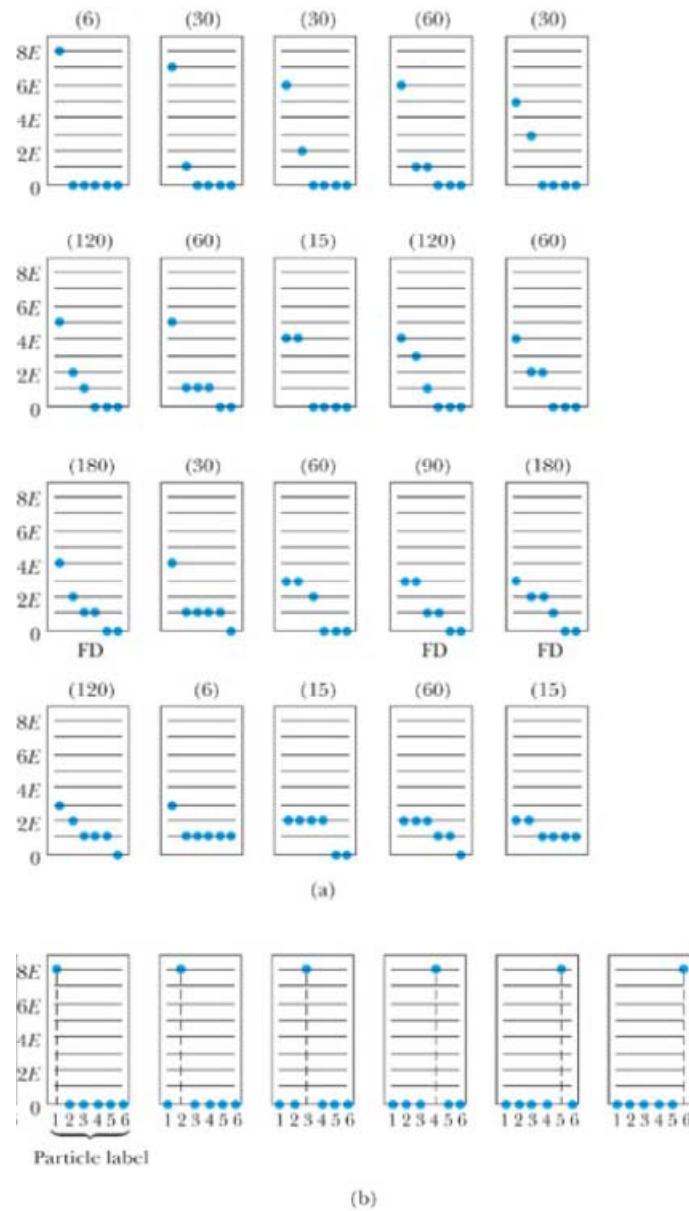
James Clerk Maxwell
(1831-1879)



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Ludwig Boltzmann
(1844-1908)





Example

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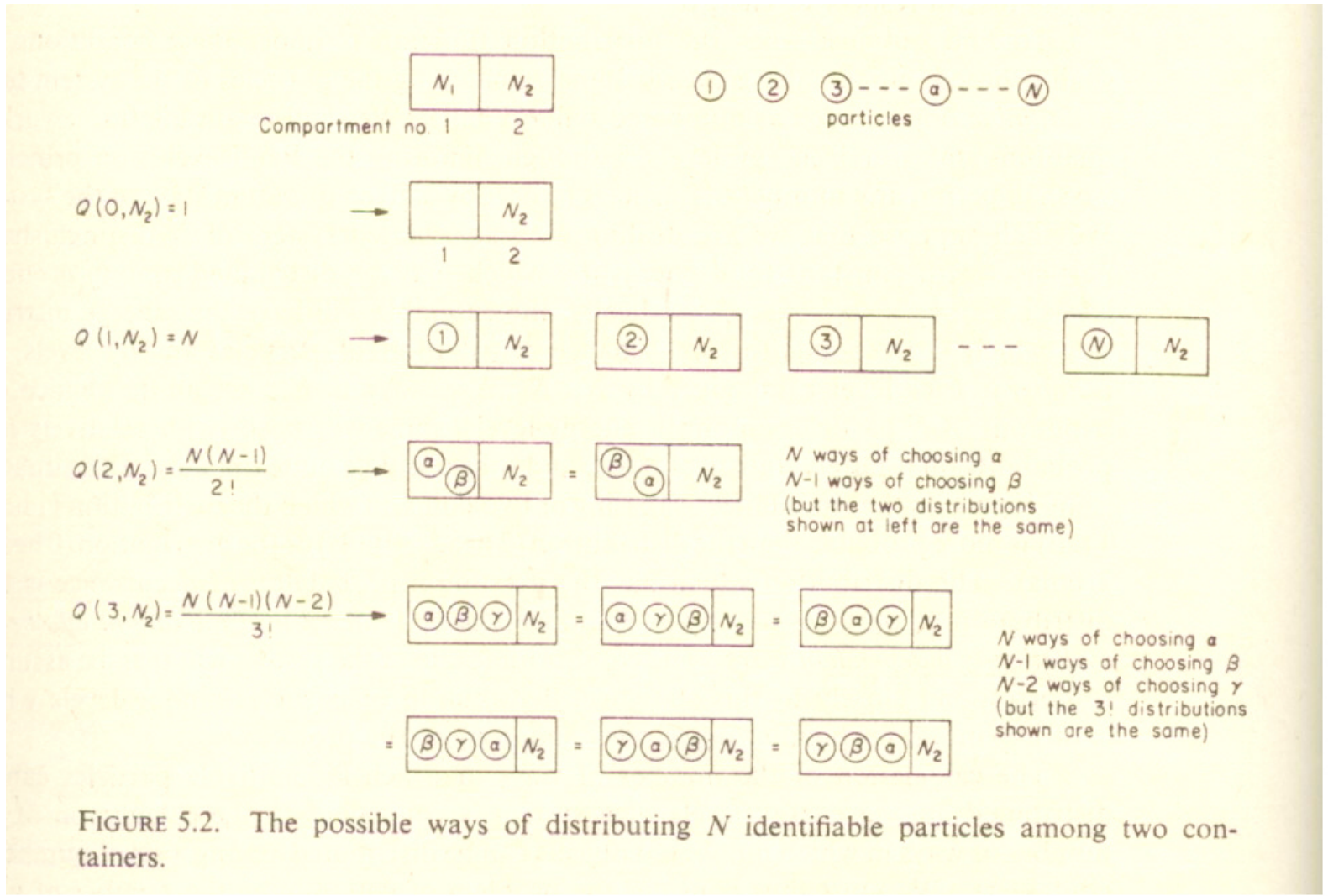


FIGURE 5.2. The possible ways of distributing N identifiable particles among two containers.



Most Probable Configuration

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

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

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

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





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

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

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

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

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





Maxwell-Boltzmann Distribution

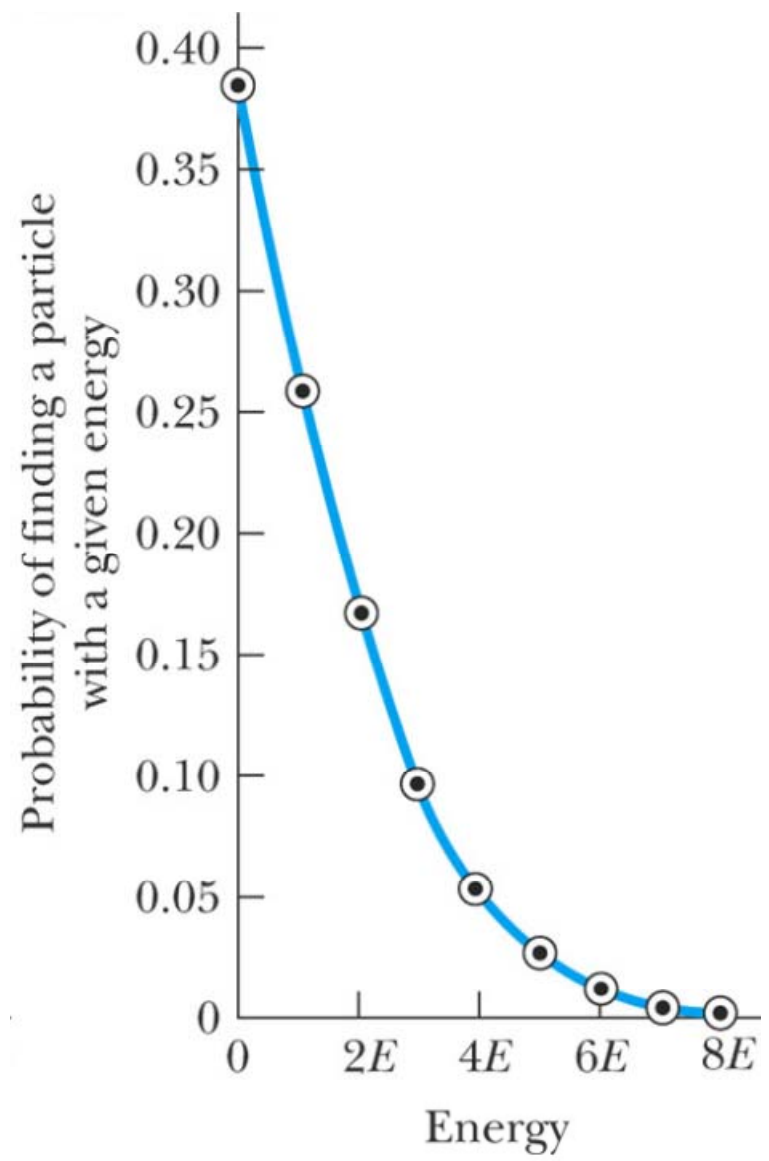
$$f_{MB}(E_i) = A \exp\left(-\frac{E_i}{k_B T}\right)$$

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

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

(경우에 따라서는 N/V 대신 N 사용)



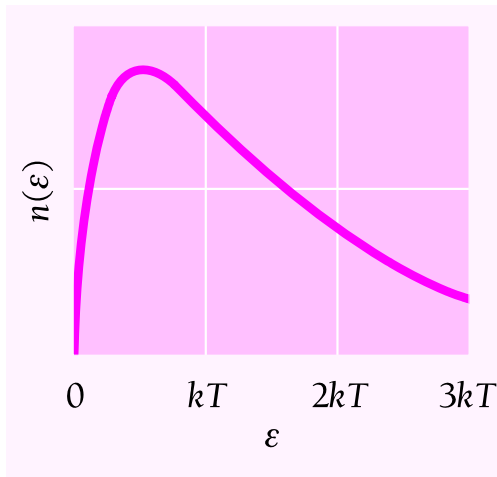
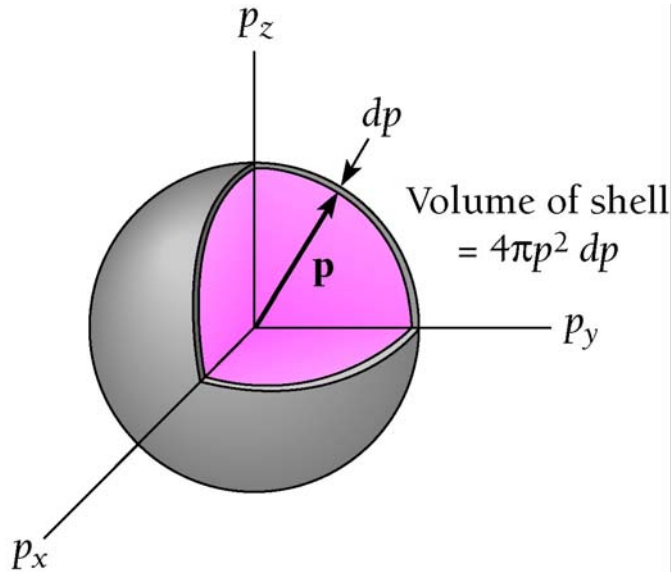


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Example



Ideal Gas



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

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

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

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

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

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

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



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

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





Equipartition of Energy

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

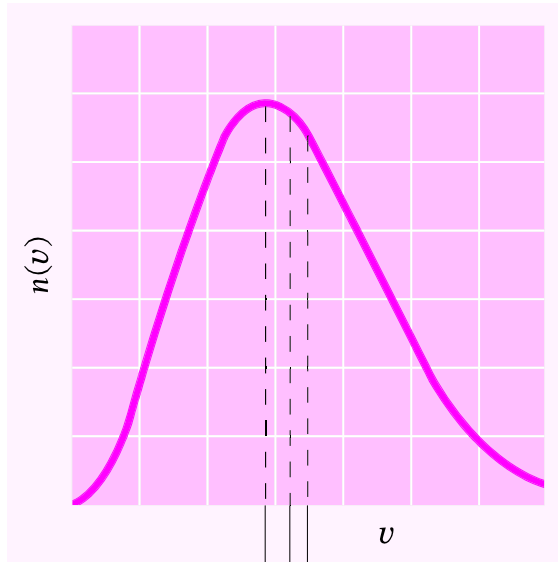
$$\frac{1}{2}m\langle v_x^2 \rangle = \frac{1}{2}m\langle v_y^2 \rangle = \frac{1}{2}m\langle v_z^2 \rangle = \frac{1}{2}k_B T$$

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



$\sqrt{v^2}$ = root-mean-square speed = $\sqrt{3kT/m}$
 \bar{v} = average speed = $\sqrt{8kT/\pi m}$
 v_p = most probable speed = $\sqrt{2kT/m}$

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

$$dE = mv dv$$

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

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





Maxwell's Speed Distribution

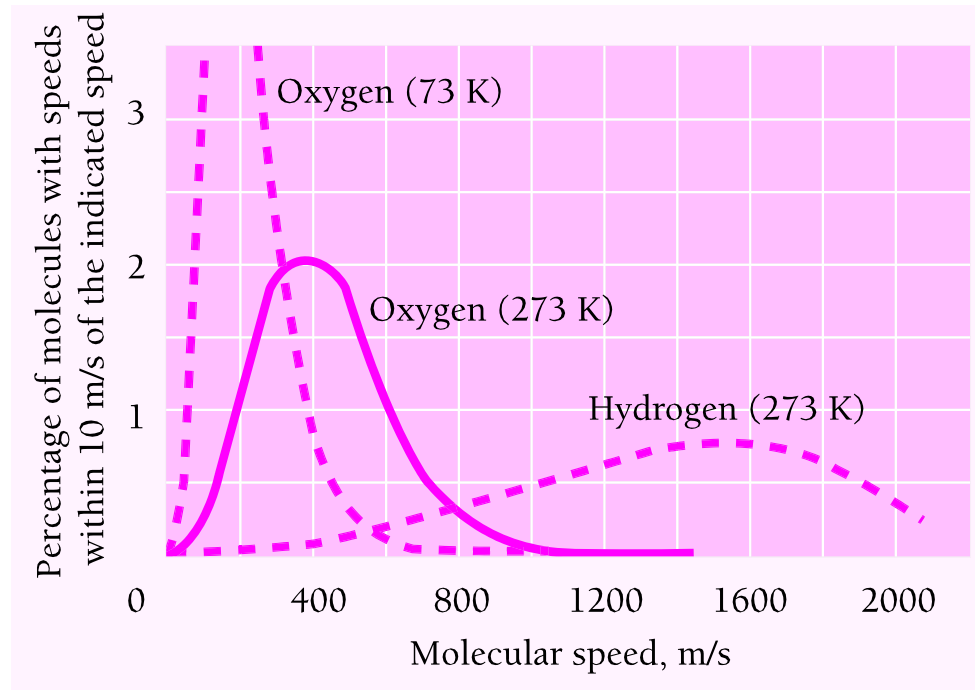


그림 9.4 73K의 산소, 273K의 산소, 그리고 273K의 수소에서의 분자 속도분포.