Chapter 2 Boltzmann Distribution

Microstates and Configurations

– Consider permutations and configurations illustrated by tossing a coin four times.

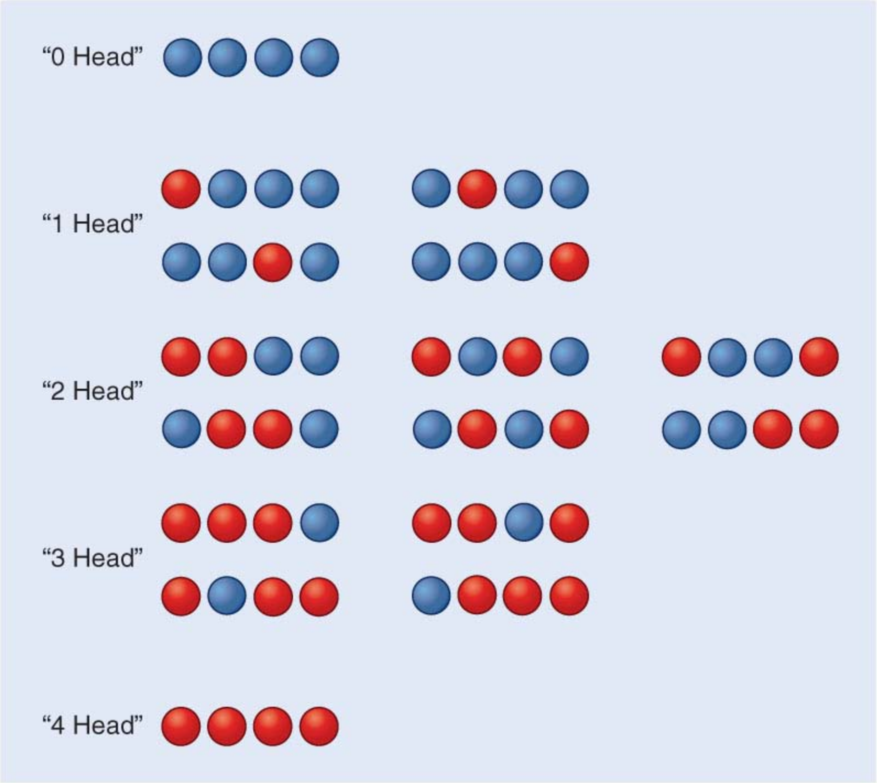


Figure 1. Possible configurations and permutations for a Bernoulli trial consisting of tossing a coin four times. Blue indicates tails and red indicates heads.

Which of these trial outcomes is most likely?

The configuration “2 Head” configuration has the greatest number of ways to achieve this configuration.

The probability (P_E) of this configuration is given by

$$P_E = \frac{E}{N}$$

where *E*: the number of permutation associated with the event of interest

N: the total number of possible permutations

The most likely configurational outcome for a trial is the configuration with the greatest number of associated permutations.

Consider a simple molecular system consisting of three quantum harmonic oscillators that share a total of three quanta of energy ($3h\nu$).

$$E_n = h\nu\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, \cdots$$

The modified energy levels of this harmonic oscillator:

$$E_n = h\nu n \qquad n = 0, 1, 2, \cdots$$

The oscillators are distinguishable.

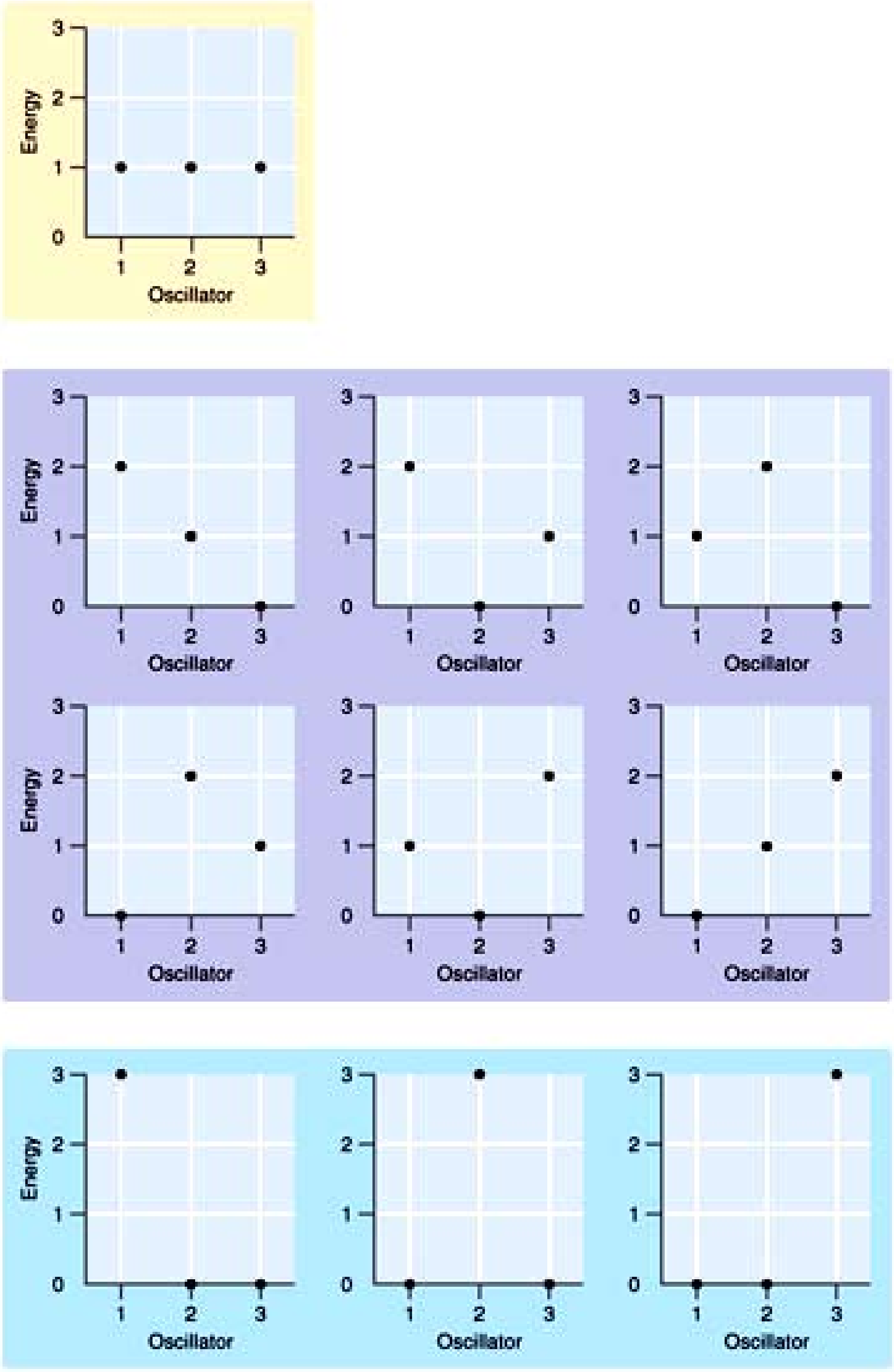


Figure 2. Configurations and associated permutations involving the distribution of three quanta of energy over three distinguishable oscillators.

configuration: a general arrangement of total energy available to the system

microstate: a specific arrangement of energy that describes the energy contained by each individual oscillator

Which configuration of energy would we expect to observe most likely?

The “2, 1, 0” configuration has a probability

$$P_E(2,1,0) = \frac{E}{N} = \frac{6}{6+3+1} = 0.6$$

Counting Microstates and Weight

The number of arrangements for N objects with a_i subgroups (the weight of the configuration) is given by

$$W\left(a_0, a_1, \cdots, a_n\right) = \frac{N!}{a_0!a_1!\cdots a_n!} = \frac{N!}{\prod_n a_n!}$$

The a_n quantities are referred to as occupation number, because they may describe how many units occupy a given energy level.

Example:

What is the weight associated with the configuration corresponding to observing 40 heads after flipping a coin 100 times?

Molecular energy levels and Boltzmann distribution

energy levels: $\varepsilon_1, \varepsilon_2, \varepsilon_3, \cdots$

↓ ↓ ↓

number of molecules: $n_1, n_2, n_3, \quad \cdots$

the configuration of the systems: the specification of the set of populations $n_1, n_2, \cdots$

e.g. i) $n_1 = N, \quad n_2 = 0, \quad n_3 = 0 \ \cdots \quad \Rightarrow$ only in one way

ii) $n_1 = N-2, \quad n_2 = 2, \quad n_3 = 0 \ \cdots \quad \Rightarrow$ more likely to occur

↓

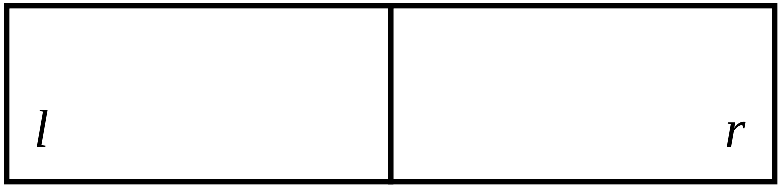
$\frac{1}{2}N(N-1)$ different ways of forming it

A general configuration $\{n_1, n_2, \ldots\}$ can be achieved in W different ways, called its weight, where

$$W(n_1, n_2, \cdots) = \frac{N!}{n_1!n_2!n_3!\cdots}$$

The Dominant configuration

Distribute N particles between left and right sides of a box



$$N_l = \frac{N}{2} + n, \qquad N_r = \frac{N}{2} - n$$

where n is deviation from the average value $\left(\frac{N}{2}\right)$.

(1) Suppose all particles are distinguishable.

Probability of N_l on left followed by N_r on right

$$= \left(\frac{1}{2}\right)^{N_l}\left(\frac{1}{2}\right)^{N_r} = \left(\frac{1}{2}\right)^{N}$$

(2) If particles are indistinguishable, then there are $\frac{N!}{N_l N_r}$ equivalent placements of particles.

$P(n)$ = the total probability

$$=\frac{\left(\frac{1}{2}\right)^N N!}{\left(\frac{N}{2}+n\right)!\left(\frac{N}{2}-n\right)!}$$

$P(0) \Rightarrow$ the maximum term

e.g. $N=6$ $\quad N_l = N_r = 3 \quad P(0)=\frac{\left(\frac{1}{2}\right)^6 6!}{3!3!}$

$N_l = 4,\ N_r = 2 \quad P(1)=\frac{\left(\frac{1}{2}\right)^6 6!}{4!2!}$

$$\frac{P(1)}{P(0)}=\frac{3}{4}$$

$N=60$ $\quad N_l = N_r = 30 \quad P(0)=\frac{\left(\frac{1}{2}\right)^{60} 60!}{30!30!}$

$N_l = 40,\ N_r = 20 \quad P(10)=\frac{\left(\frac{1}{2}\right)^{60} 60!}{40!20!}$

$$\frac{P(10)}{P(0)}=\frac{(30!)^2}{40!20!}\cong 3.4\times 10^{-34}$$

Toss a coin 10 times.

$$N = 10 \qquad N_H = N_T = 5 \qquad P(N_H = 50\%) = \frac{\left(\tfrac{1}{2}\right)^{10} 10!}{5!5!}$$

$$N_H = 4,\ N_T = 6 \qquad P(N_H = 40\%) = \frac{\left(\tfrac{1}{2}\right)^{10} 10!}{6!4!}$$

$$\frac{P\left(N_H = 40\%\right)}{P\left(N_H = 50\%\right)} = \frac{5!5!}{6!4!} = \frac{5}{6} = 0.833$$

$$N = 100 \qquad N_H = N_T = 50 \qquad P(N_H = 50\%) = \frac{\left(\tfrac{1}{2}\right)^{100} 100!}{50!50!}$$

$$N_H = 40,\ N_T = 60 \qquad P(N_H = 40\%) = \frac{\left(\tfrac{1}{2}\right)^{100} 100!}{60!40!}$$

$$\frac{P\left(N_H = 40\%\right)}{P\left(N_H = 50\%\right)} = \frac{50!50!}{60!40!} \cong 0.136$$

The configuration associated with observing 50% heads should become dominant configuration as the number of coin tosses increases.

Indeed, the most probable configuration evolves into the dominant configuration as the size the system increases.

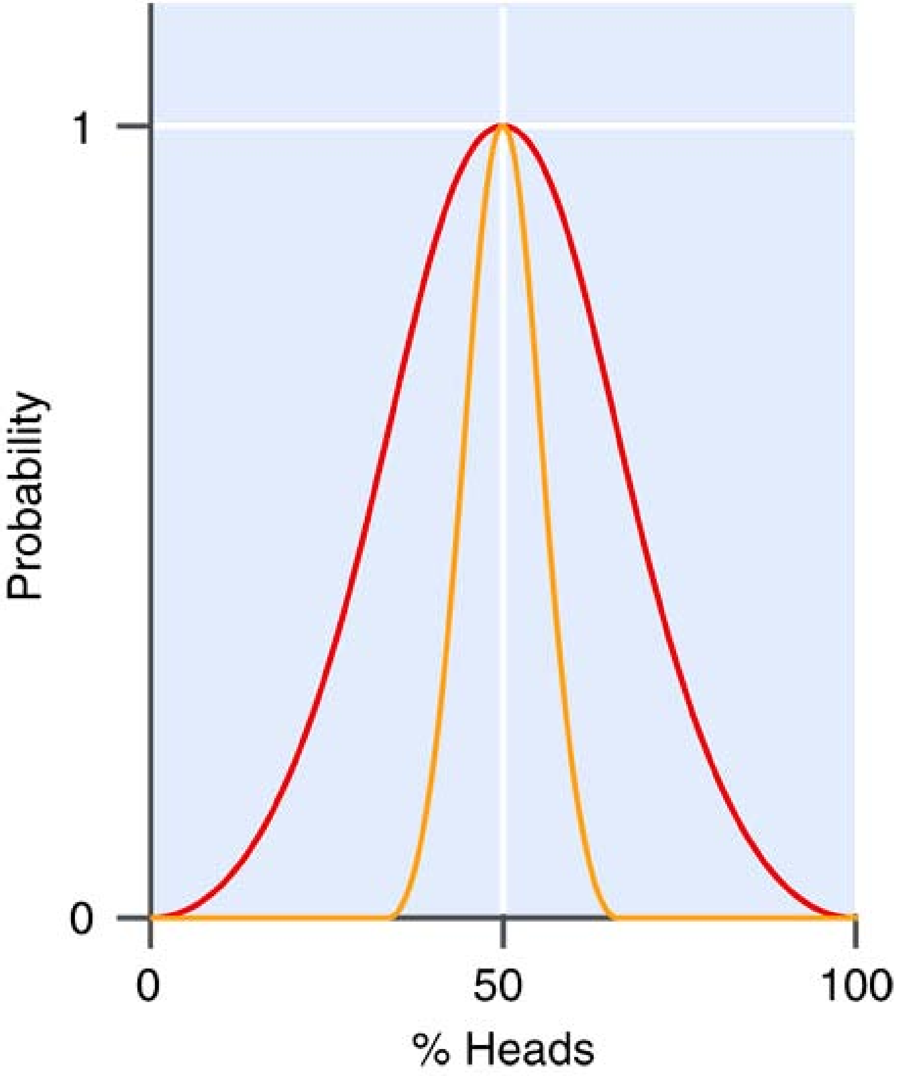


Figure 3. Comparison of relative probability for outcomes of a coin-flip trial in which the number of tosses is 10 (red line) and 100 (yellow line). Notice that all trials have a maximum probability at 50 % heads; however, as the number of tosses increases, the probability distribution becomes more centered about this value as evidenced by the decrease in distribution width.

Example:

Consider a collection of 10,000 particles with each particle capable of populating one of three energy levels having energies, 0, ε, and 2ε with a total available energy of 5000ε. Under the constraint that the total number of particles and total energy be constant, determine the dominant configuration.

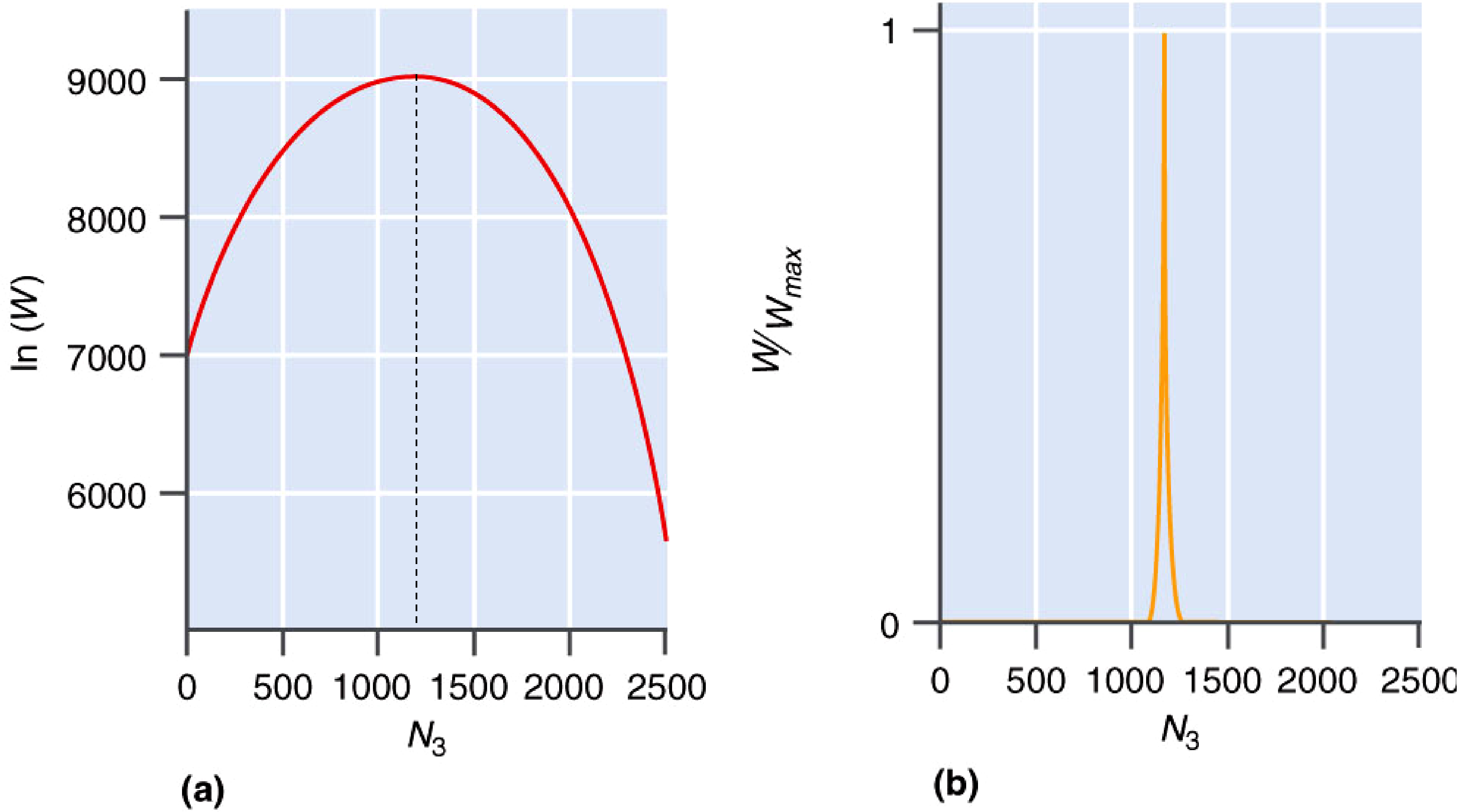


Figure 4. Illustration of the dominant configuration for a system consisting of 10,000 particles with each particle having three energy levels at energies of 0, ε, and 2ε as discussed in Example. The number of particles populating the higher energy level is N_3, and the energy configurations are characterized by the population in this level. **(a)** Variation in the natural log of the weight, ln(*W*), for energy configurations as a function of N_3, demonstrating that ln(*W*) has a maximum at $N_3 = 1200$. **(b)** Variation in the weight associated with a given configuration to that of the dominant configuration.

Derivation of the Boltzmann Distribution

W: – the weight of the configuration

– the total number of microstates associated with a given configuration of energy

Because W will be large for molecular systems, it is more convenient to work with $\ln W$, and the search criterion for the dominant configuration becomes

$$\frac{d\ln W}{d\,a_n} = 0 \quad \text{for all } a_n, \qquad W = \frac{N!}{\prod_n a_n!}$$

$$\ln W = \ln N! - \ln \prod_n a_n! = N\ln N - \sum_n a_n \ln a_n$$

$$\frac{\partial \ln W}{\partial a_n} = \frac{\partial N}{\partial a_n}\ln N + N\frac{\partial \ln N}{\partial a_n} - \sum_n \frac{\partial (a_n \ln a_n)}{\partial a_n}$$

$$= \ln N + N\left(\frac{1}{N}\right) - \left(\ln a_n + 1\right) = -\ln\left(\frac{a_n}{N}\right)$$

Note: $N = \sum_n a_n$

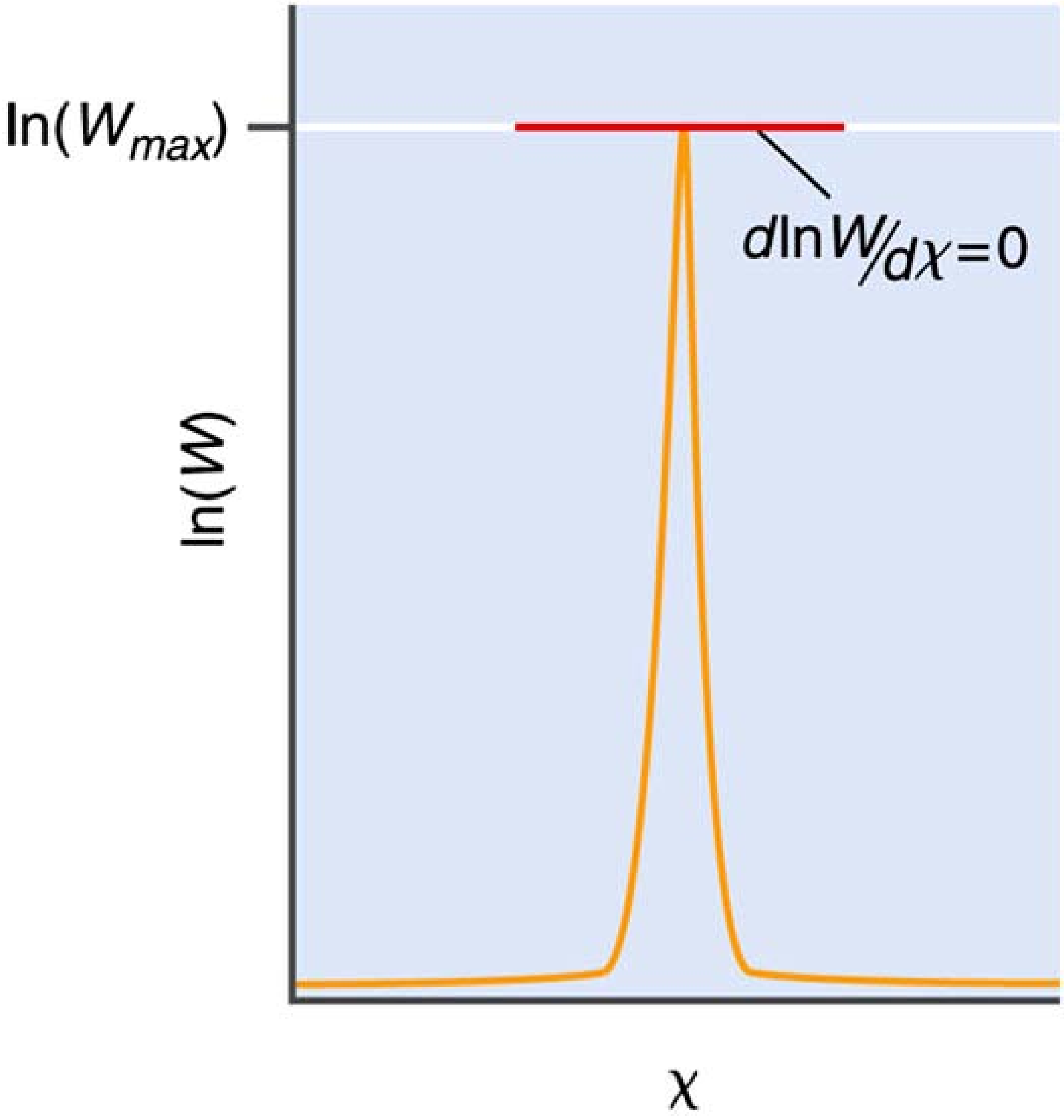


Figure 4-1. Mathematical definition of the dominant configuration.

Restrictive condition:

1. $a_1 + a_2 + \cdots\cdots = \sum a_n = N$ a constant

2. $a_1\varepsilon_1 + a_2\varepsilon_2 + \cdots\cdots = \sum a_n\varepsilon_n = E$ a constant

$$\delta \ln W = \left(\frac{\partial \ln W}{\partial a_1}\right)\delta a_1 + \left(\frac{\partial \ln W}{\partial a_2}\right)\delta a_2 + \cdots\cdots + \left(\frac{\partial \ln W}{\partial a_n}\right)\delta a_n + \cdots\cdots \qquad (*)$$

From the restriction 1,

$$\delta a_1 + \delta a_2 + \cdots\cdots + \delta a_n + \cdots\cdots = \delta N = 0 \qquad (**)$$

From the restriction 2,

$$\varepsilon_1\delta a_1 + \varepsilon_2\delta a_2 + \cdots\cdots + \varepsilon_n\delta a_n + \cdots\cdots = \delta E = 0 \qquad (***)$$

Lagrange's method of undetermined multipliers

$$\mathrm{eq}\,(*) + \mathrm{eq}\,(**) \times \alpha + \mathrm{eq}\,(***) \times (-\beta)$$

$$\delta \ln W = \left(\frac{\partial \ln W}{\partial a_1} + \alpha - \beta \varepsilon_1 \right) \delta a_1 + \left(\frac{\partial \ln W}{\partial a_2} + \alpha - \beta \varepsilon_2 \right) \delta a_2 + \cdots$$

$$+ \left(\frac{\partial \ln W}{\partial a_n} + \alpha - \beta \varepsilon_n \right) \delta a_n + \cdots \qquad \text{(a)}$$

When δ ln$W$=0, ln$W$ has a maximum value.

Since eq (a) holds for any α and β, but we choose values of α and β such that

$$\frac{\partial \ln W}{\partial a_1} + \alpha - \beta \varepsilon_1 = 0$$

$$\frac{\partial \ln W}{\partial a_2} + \alpha - \beta \varepsilon_2 = 0$$

Then,

$$\delta \ln W = \left(\frac{\partial \ln W}{\partial a_3} + \alpha - \beta \varepsilon_3 \right) \delta a_3 + \left(\frac{\partial \ln W}{\partial a_4} + \alpha - \beta \varepsilon_4 \right) \delta a_4 + \cdots$$

$$+ \left(\frac{\partial \ln W}{\partial a_n} + \alpha - \beta \varepsilon_n \right) \delta a_n + \cdots = 0 \qquad \text{(b)}$$

where the values of δa_3, $\delta a_4, \cdots$, $\delta a_n, \cdots$ can be chosen independently.

The only way of ensuring the right-hand side of eq (b) is zero for any small value of δa_3, $\delta a_4, \cdots$ is to equate all the quantities in brackets to zero, i.e.,

$$\frac{\partial \ln W}{\partial a_3} + \alpha - \beta \varepsilon_3 = 0$$

$$\frac{\partial \ln W}{\partial a_4} + \alpha - \beta \varepsilon_4 = 0$$

$$\vdots$$

$$\frac{\partial \ln W}{\partial a_n} + \alpha - \beta \varepsilon_n = 0 \qquad n = 1,\ 2,\ 3$$

Since $\frac{\partial \ln W}{\partial a_n} = -\ln\left(\frac{a_n}{N}\right)$,

$$-\ln\left(\frac{a_n}{N}\right) + \alpha - \beta\varepsilon_n = 0$$

$$\ln\left(\frac{a_n}{N}\right) = \alpha - \beta\varepsilon_n$$

$$\boldsymbol{\frac{a_n}{N} = e^{\alpha} e^{-\beta\varepsilon_n}}$$

$$a_n = N e^{\alpha} e^{-\beta\varepsilon_n}$$

$$N = \sum_n a_n = \sum_n N e^{\alpha} e^{-\beta\varepsilon_n} = N e^{\alpha} \sum_n e^{-\beta\varepsilon_n}$$

$$1 = e^{\alpha} \sum_n e^{-\beta\varepsilon_n}$$

$$e^{\alpha} = \frac{1}{\sum_n e^{-\beta\varepsilon_n}}$$

$\boldsymbol{q = \sum_n e^{-\beta\varepsilon_n}}$ **:** the partition function

The partition function represents the sum over all terms that describes the probability associated with the variable of interest, in this case ε_n or the energy level n.

The probability of occupying a given energy level (P_n) is given by

$$\boldsymbol{P_n = \frac{a_n}{N} = e^{\alpha} e^{-\beta\varepsilon_n} = \frac{e^{-\beta\varepsilon_n}}{\sum_n e^{-\beta\varepsilon_n}}}$$

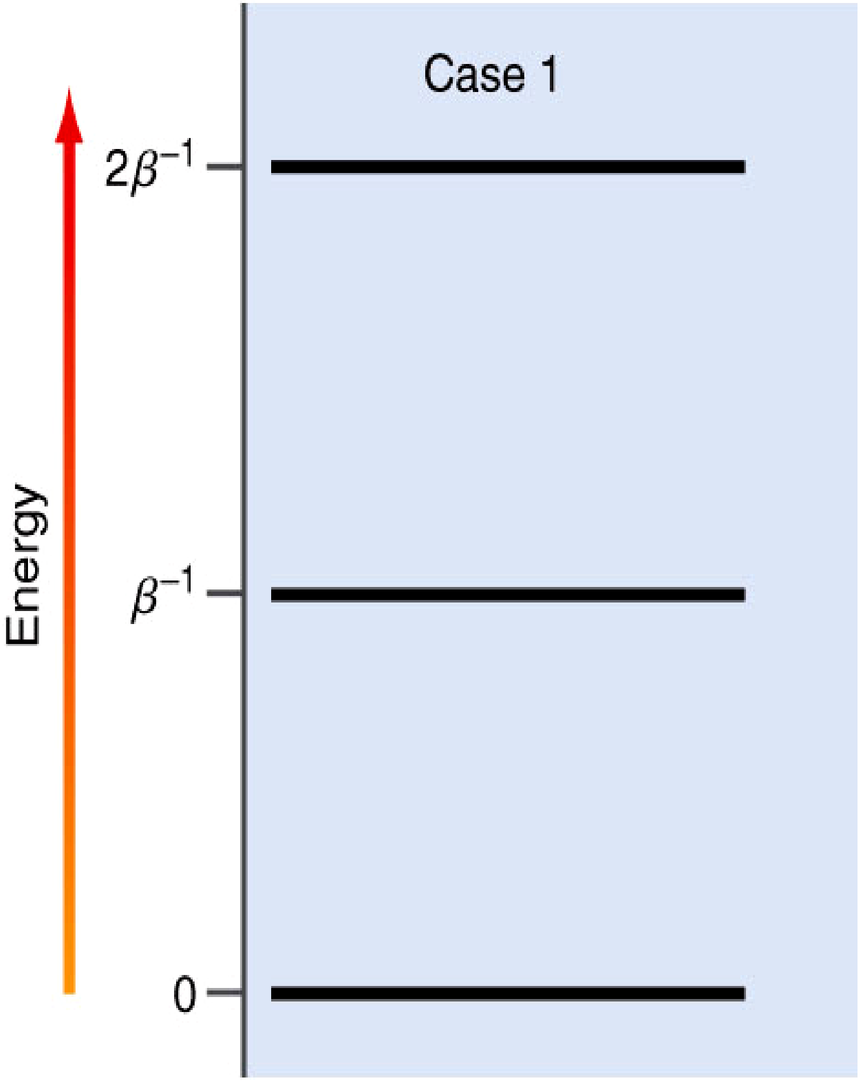
This quantitatively describes the probability of occupying a given energy for the dominant configuration of energy. This well-known and important result is referred to as the Boltzmann distribution.

Assume $\beta = \dfrac{1}{h\nu}$.

The energy levels of the harmonic oscillator are $\varepsilon_n = nh\nu$ for $n = 0,1,2,\cdots$

$$e^{-\beta\varepsilon_n} = e^{-\frac{nh\nu}{h\nu}} = e^{-n}$$

An oscillator occupying the first three levels



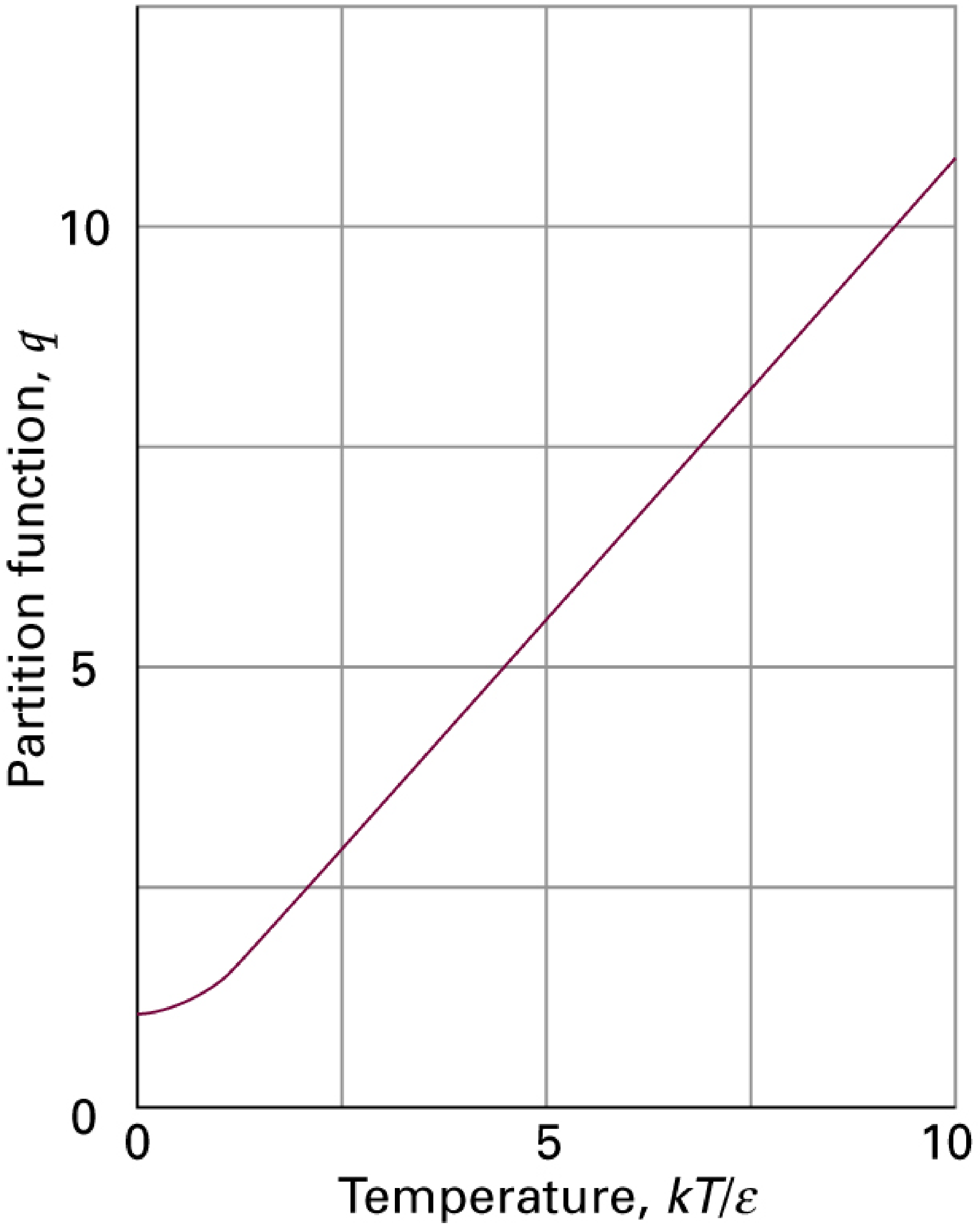
$$\therefore q = \sum_n e^{-\beta\varepsilon_n} = \sum_n e^{-n} = \frac{1}{1-e^{-1}} = 1.58$$

$$\left(\because e^{-1} < 1\right)$$

$$P_0 = \frac{e^{-\beta\varepsilon_0}}{q} = \frac{e^{0}}{1.58} = 0.633$$

$$P_1 = \frac{e^{-\beta\varepsilon_1}}{q} = \frac{e^{-\frac{h\nu}{h\nu}}}{q} = \frac{e^{-1}}{1.58} = 0.233$$

$$P_2 = \frac{e^{-\beta\varepsilon_2}}{q} = \frac{e^{-\frac{2h\nu}{h\nu}}}{q} = \frac{e^{-2}}{1.58} = 0.086$$



$$q = \sum e^{-\beta\varepsilon} = \frac{1}{1 - e^{-\beta\varepsilon}}$$

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

Figure 4-2.
The partition function for the system of a harmonic oscillator as a function of temperature.

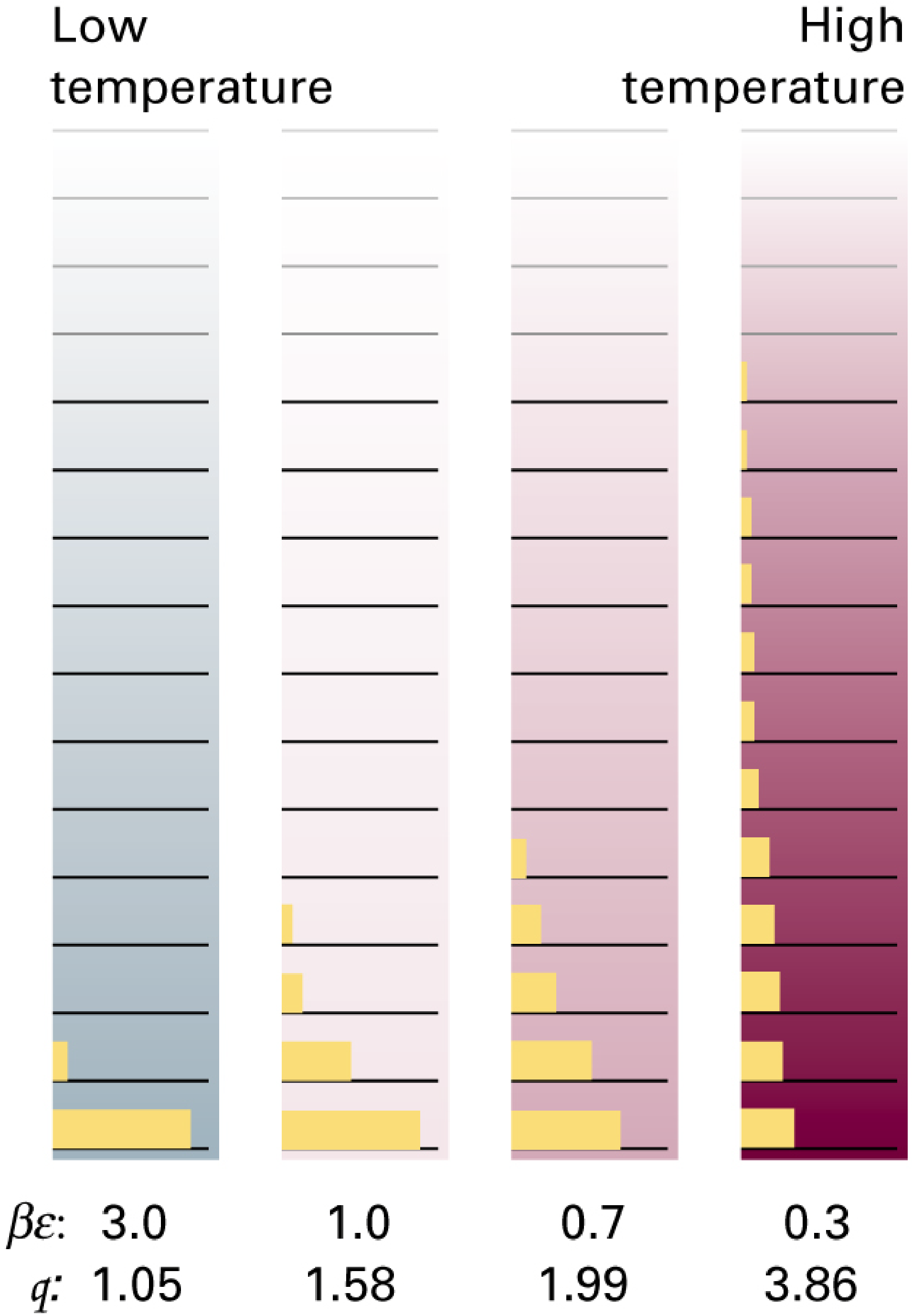


Figure 4-3.
Populations of molecular states at various temperatures.

Degeneracy

degeneracy: multiple states at a given energy level

$$q = \sum_n g_n e^{-\beta\varepsilon_n} \qquad q = \sum_n e^{-\beta\varepsilon_n}$$

$$P_i = \frac{g_i e^{-\beta\varepsilon_i}}{q}, \quad \text{where } g_i \text{ is the degeneracy of the energy level } i.$$

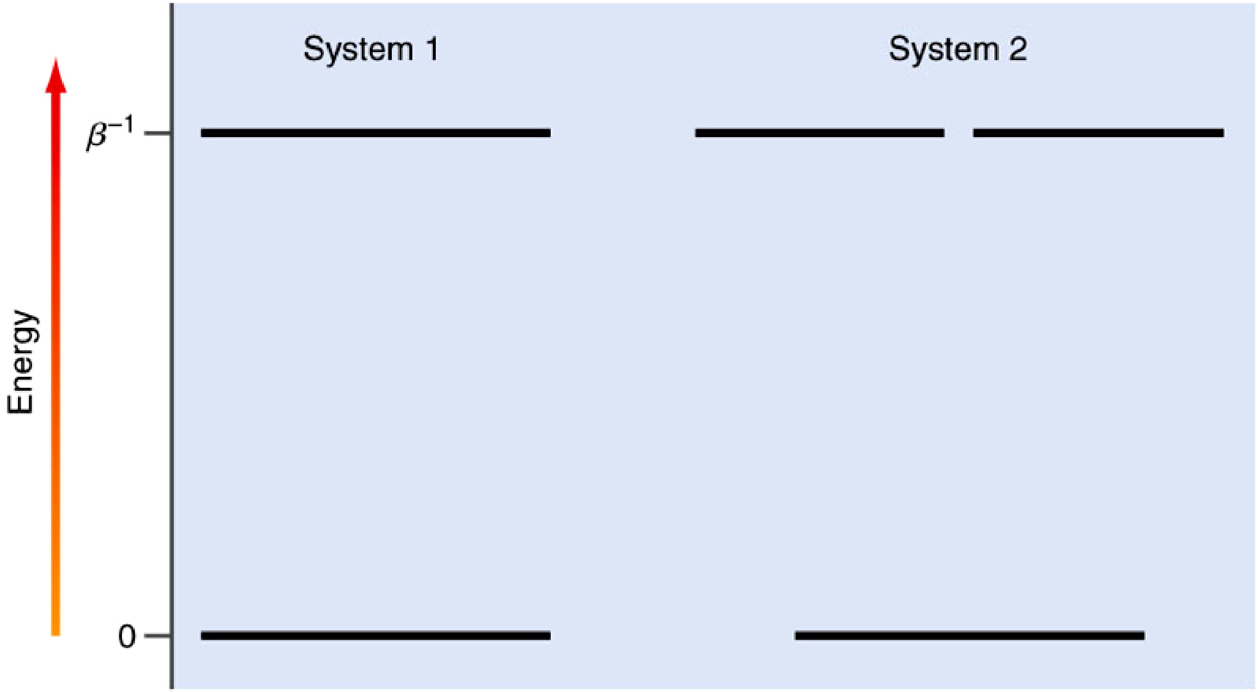


Figure 5. Illustration of degeneracy. In system 1, one state is present at energies 0 and β^{-1}. In system 2, the energy spacing is the same, but at energy β^{-1} two states are present such that the degeneracy at this energy is two.

Consider Figure 5.

The partition function for the first system

$$q(1) = \sum_n g_n e^{-\beta\varepsilon_n} = 1 + e^{-1} = 1.34$$

The partition function for the second system

$$q(2) = \sum_n g_n e^{-\beta\varepsilon_n} = 1 + 2e^{-1} = 1.74$$

The corresponding probability of occupying a state at energy β^{-1} for the two systems

$$P_1(1) = \frac{g_1 e^{-\beta\varepsilon_1}}{q} = \frac{e^{-1}}{1.34} = 0.27$$

$$P_1(2) = \frac{g_i e^{-\beta\varepsilon_i}}{q} = \frac{2e^{-1}}{1.74} = 0.42$$

Dominance of the Boltzmann Distribution

$W_{\max}$: the largest number of microstates

Consider a slight different configuration having weight (=W) and $W<W_{\max}$.

Let α_n be the fractional change in the number of units present in the nth state:

$$\alpha_n = \frac{a_n' - a_n}{a_n} = \frac{\delta_n}{a_n}$$

$$\Delta N = 0,\ \ \Delta E = 0$$

$$\frac{W_{\max}}{W} = \frac{\dfrac{N!}{\prod\limits_n a_n!}}{\dfrac{N!}{\prod\limits_n (a_n+\delta_n)!}} = \prod_n \left(a_n + \frac{\delta_n}{2} \right)^{\delta_n},\ \text{ when } |\delta_n| \ll a_n.$$

$$\ln\left(\frac{W_{\max}}{W}\right)=\sum_n \ln\left(a_n+\frac{\delta_n}{2}\right)^{\delta_n}$$

$$=\sum_n \delta_n \ln\left(a_n+\frac{\delta_n}{2}\right)$$

$$=\sum_n \delta_n \ln a_n\left(1+\frac{\delta_n}{2a_n}\right)$$

$$=\sum_n \delta_n \ln a_n+\sum_n \delta_n \ln\left(1+\frac{\delta_n}{2a_n}\right)$$

$$\therefore \ln\left(\frac{W_{\max}}{W}\right)=\sum_n \delta_n \ln a_n+\sum_n \frac{\delta_n^{\,2}}{2a_n}$$

$\ln(1\pm z)\cong \pm z$ for $z \ll 1$

Recall the following definition, which related the fractional change in occupation number to the occupation numbers itself:

$$\alpha_n=\frac{\delta_n}{a_n}$$

$$\therefore\ \ln\left(\frac{W_{\max}}{W}\right)=\sum_n \alpha_n a_n \ln a_n+\sum_n \frac{a_n}{2}\left(\alpha_n^2\right)$$

$$=\sum_n \alpha_n a_n\left(\ln a_0-\beta\varepsilon_n\right)+\sum_n \frac{a_n}{2}\left(\alpha_n^2\right)$$

$$\frac{a_n}{N}=e^{\alpha}e^{-\beta\varepsilon_n}$$

$$=\sum_n \alpha_n a_n \ln a_0-\sum_n \beta\varepsilon_n\alpha_n a_n+\sum_n \frac{a_n}{2}\left(\alpha_n^2\right)$$

$$=\sum_n \alpha_n a_n \ln a_0-\beta\sum_n \varepsilon_n\alpha_n a_n+\sum_n \frac{a_n}{2}\left(\alpha_n^2\right)$$

$$=\sum_n \frac{a_n}{2}\left(\alpha_n^2\right)$$

$$\left(\because\ \Delta N=\sum_n \alpha_n a_n=0;\ \Delta E=\sum_n \varepsilon_n\alpha_n a_n=0\right)$$

The root-mean-squared deviation in occupation number is defined as

$$\alpha_{rms}=\sqrt{\frac{\sum_n a_n\alpha_n{}^2}{N}}$$

$$\therefore\frac{W_{\max}}{W}=e^{\sum_n \frac{a_n}{2}\left(\alpha_n{}^2\right)}=e^{\frac{N\alpha_{rms}{}^2}{2}}$$

For an example,

$$N = 1 \text{ mole} = 6.022 \times 10^{23}$$

$$\alpha_{rms} = 10^{-10}$$

$$\frac{W_{\max}}{W} = e^{\frac{\left(6.022 \times 10^{23}\right)\left(10^{-20}\right)}{2}} \approx e^{3000}$$

The ratio of weights is extremely large number, and it demonstrates that a minute change in configuration will result in significant reduction weight. Clearly, the width of the curve illustrated in Figure 4-1 is extremely small in the a system where *N* is on the order of Avogadro's number, and the most probable distribution is virtually the only distribution that will be observed for a macroscopic assembly of units.

The Definition of β

$$\ln W = \ln N! - \ln \prod_n a_n!$$

$$= \ln N! - \sum_n \ln a_n!$$

$$d\ln W = -\sum_n d\ln a_n!$$

$$= -\sum_n d(a_n \ln a_n - a_n)$$

$$= -\sum_n \left(\ln a_n da_n + \cancel{a}_n \frac{d\cancel{a}_n}{\cancel{a}_n} - d\cancel{a}_n \right)$$

$$= -\sum_n \ln a_n da_n$$

The ratio of the occupation number for an arbitrary energy level, ε_n, to the lowest or ground energy level (ε_n=0):

$$\frac{a_n}{a_0} = \frac{\dfrac{Ne^{-\beta\varepsilon_n}}{q}}{\dfrac{Ne^{-\beta\varepsilon_0}}{q}} = e^{-\beta\varepsilon_n} \Rightarrow \ln a_n = \ln a_0 - \beta\varepsilon_n$$

$$\therefore d\ln W = -\sum_n \left(\ln a_0 - \beta\varepsilon_n\right) da_n$$

$$= -\ln a_0 \underbrace{\sum_n \cancel{da_n}}_{0} + \beta \sum_n \varepsilon_n da_n = \beta \sum_n \varepsilon_n da_n$$

($\because$ For a closed system, $dN = 0$.)

$$\sum_n \varepsilon_n da_n = dE$$

$$\therefore d\ln W = \beta dE$$

Imagine two separate systems of distinguishable units at equilibrium having associated weights W_x and W_y.

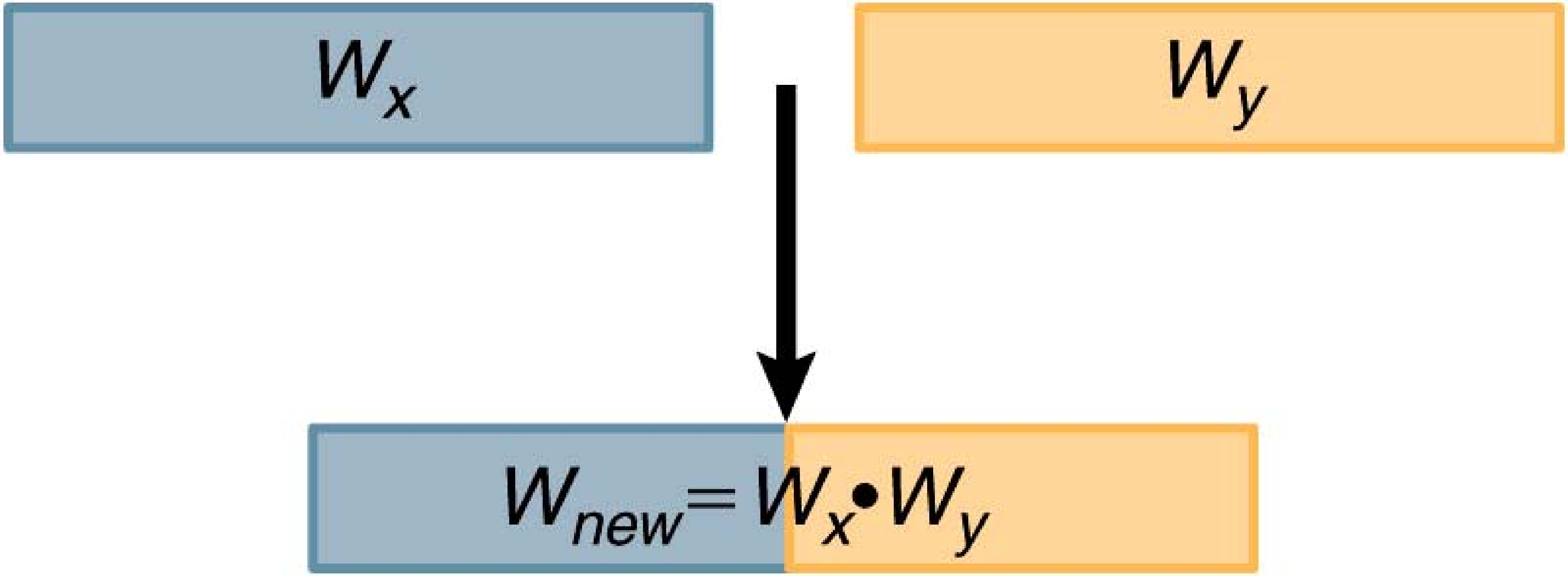


Figure 6. Two assemblies of distinguishable units, denoted x and y, are brought into thermal contact.

If the two systems are initially at different equilibrium conditions, the instantaneous composite system weight will be less than the weight of the composite system at equilibrium. Since the composite weight will increase as equilibrium is approached,

$$d(W_x \cdot W_y) \geq 0$$

$$\therefore W_x dW_x + W_y dW_y \geq 0$$

$$\frac{dW_x}{W_x} + \frac{dW_y}{W_y} \geq 0$$

$$d \ln W_x + d \ln W_y \geq 0$$

$$\therefore \beta_x dE_x + \beta_y dE_y \geq 0$$

$$d \ln W = \beta dE$$

When the composite system is isolated from surroundings,

$$dE_x + dE_y = 0$$

$$dE_x = -dE_y$$

If dE_x is positive,

$$\beta_x \geq \beta_y$$

$$dE_x > 0 \quad \rightarrow \quad T_y > T_x$$

$$\therefore \beta \propto \frac{1}{T}$$

$$\beta = \frac{1}{kT} \qquad (\leftarrow d\ln W = \beta dE)$$

k: Boltzmann’s constant = 1.381 x 10^{-23} J/K

Example:

The vibrational frequency of I_2 is 208 cm^{-1}. What is the probability of I_2 populating the $n=2$ vibrational level if the molecular temperature is 298 K?

This result is then used to evaluate the probability of occupying the second vibrational state (n=2) as follows:

$$P_2 = \frac{e^{-2\beta hc\tilde{\nu}}}{q}$$

$$= \frac{\exp\left[-2\left(\frac{(6.626\times10^{-34}\ \mathrm{J\,s})(3.00\times10^{10}\ \mathrm{cm\,s^{-1}})(208\,\mathrm{cm^{-1}})}{(1.38\times10^{-23}\ J/K)(298\,K)}\right)\right]}{1.58}$$

$$= 0.086$$