

**Simple harmonics: multiplicity**  
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Here we discuss the thermodynamic properties of simple harmonic systems using the approach of microcanonical ensemble. For the system with  $f$  simple harmonics, we need to discuss the multiplicity (corresponding to the density of states) for each energy level. Once the multiplicity is evaluated, the entropy and temperature can be determined along the approach of microcanonical ensemble.

**1. Energy separation (different)**

**(a) One particle system**

The separation energy is different. For simplicity we consider only the three energy levels.


$$\text{-----} \varepsilon_3 (y)$$

$$\text{-----} \varepsilon_2 (x)$$

$$\text{-----} \varepsilon_1 (1)$$

$$(1 + x + y) = 1 + x + y$$

There are 3 states.

$(\varepsilon_1)$	multiplicity = coefficient of 1 = 1
$(\varepsilon_2)$	multiplicity = coefficient of $x$ = 1
$(\varepsilon_3)$	multiplicity = coefficient of $y$ = 1

**(b). The two particle system:**

$$(1 + x + y)^2 = 1 + 2x + x^2 + 2y + 2xy + y^2$$

There are  $3^2 = 9$  states.

$(\varepsilon_1, \varepsilon_1)$	multiplicity = coefficient of $1 = 1$
$(\varepsilon_2, \varepsilon_2)$	multiplicity = coefficient of $x^2 = 1$
$(\varepsilon_3, \varepsilon_3)$	multiplicity = coefficient of $y^2 = 1$
$(\varepsilon_1, \varepsilon_2)$	multiplicity = coefficient of $x = 2$
$(\varepsilon_1, \varepsilon_3)$	multiplicity = coefficient of $y = 2$
$(\varepsilon_2, \varepsilon_3)$	multiplicity = coefficient of $xy = 2$

**(c) The three particle system:**

$$(1 + x + y)^3 = 1 + 3x + 3x^2 + x^3 + 3y + 6xy + 3x^2y + 3y^2 + 3xy^2 + y^3$$

**(d). The four particle system:**

$$(1 + x + y)^4 = 1 + 4x + 6x^2 + 4x^3 + x^4 + 4y + 12xy + 12x^2y + 4x^3y + 6y^2 + 12xy^2 + 6x^2y^2 + 4y^3 + 4xy^3 + y^4$$

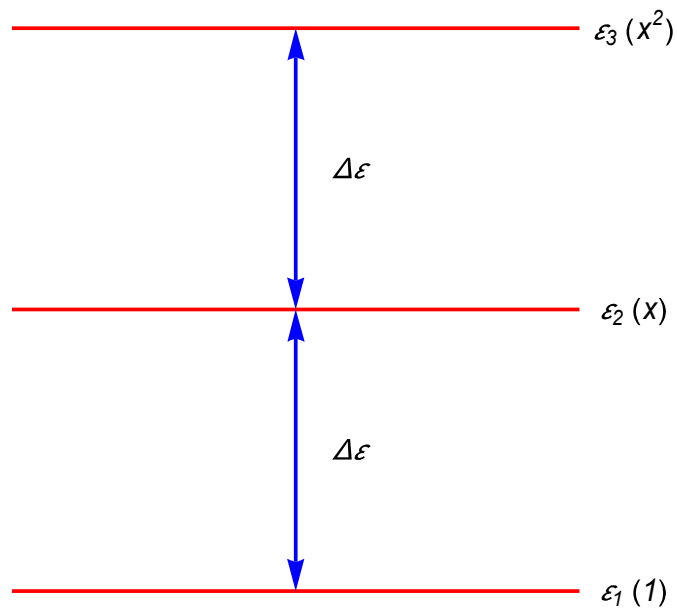
**(e)  $n$  particle system**

In general, for the  $n$ -particle system

$$(1 + x + y)^n$$

**2. The separation energy (the same)**

We consider that the energy separation is the same.



**(a) One particle system**

$$(1 + x + x^2)^2 = 1 + 2x + 3x^2 + 2x^3 + x^4$$

There are  $3^2 = 9$  states.

$(\varepsilon_1, \varepsilon_1)$	multiplicity = coefficient of $1 = 1$	(energy = 0)
$(\varepsilon_2, \varepsilon_2)$	multiplicity = coefficient of $x^2 = 1$	(energy = $2\Delta\varepsilon$ )
$(\varepsilon_3, \varepsilon_3)$	multiplicity = coefficient of $x^4 = 1$	(energy = $4\Delta\varepsilon$ )
$(\varepsilon_1, \varepsilon_2)$	multiplicity = coefficient of $x = 2$	(energy = $\Delta\varepsilon$ )
$(\varepsilon_1, \varepsilon_3)$	multiplicity = coefficient of $x^2 = 2$	(energy = $2\Delta\varepsilon$ )
$(\varepsilon_2, \varepsilon_3)$	multiplicity = coefficient of $x^3 = 2$	(energy = $3\Delta\varepsilon$ )

**(b) The two particle system (with two energy levels)**

—————  $\varepsilon_2$  (degeneracy:  $g_2$ )

—————  $\varepsilon_1$  (degeneracy  $g_1$ )

$$(g_1 + g_2 x)^2 = g_1^2 + g_2^2 x^2 + 2g_1 g_2 x$$

$(\varepsilon_1, \varepsilon_1)$	multiplicity = coefficient of $1 = g_1^2$	(energy = 0)
$(\varepsilon_1, \varepsilon_2)$	multiplicity = coefficient of $x = 2g_1 g_2$	(energy = $\Delta\varepsilon$ )
$(\varepsilon_1, \varepsilon_2)$	multiplicity = coefficient of $x^2 = g_2^2$	(energy = $2\Delta\varepsilon$ )

### 3. Simple harmonics

We discuss the multiplicity function for harmonic oscillators

Harmonic oscillator (one system):

$$H = \frac{1}{2m} p^2 + \frac{1}{2} m \omega^2 q^2 \quad (\text{Hamiltonian})$$

The quantum state of a harmonic oscillator:

$$\hat{H}|s\rangle = \hbar\omega(s + \frac{1}{2})|s\rangle$$

$s$  is a positive integer or zero.  $\omega$  is the angular frequency of the oscillator. The number of states is infinite and multiplicity of each state is one. Now we consider a system of  $N$  such oscillators, all of the same angular frequency. We consider the multiplicity function  $g(N, n)$  for the  $N$  oscillators.

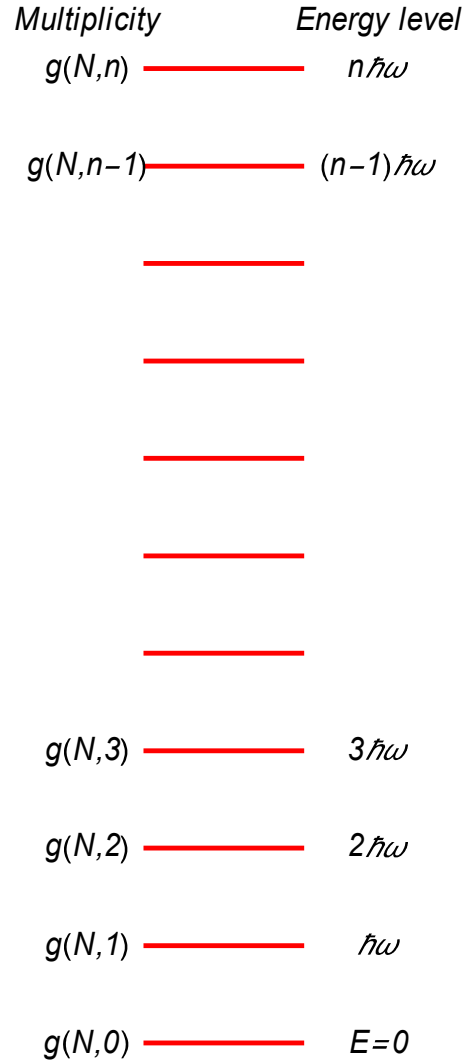
$$E = n\hbar\omega + \frac{N}{2}\hbar\omega = (s_1 + s_2 + \dots + s_N)\hbar\omega + \frac{N}{2}\hbar\omega$$

or

$$s_1 + s_2 + \dots + s_N = n$$

where  $\frac{N}{2}\hbar\omega$  is the zero point energy of the simple harmonics (quantum mechanics in origin),

$$0 \leq s_1 < \infty, \quad 0 \leq s_2 < \infty, \dots, \quad 0 \leq s_N < \infty$$



**Fig.** Energy level and the multiplicity for the system with the energy  $E = n\hbar\omega$ , where the zero point energy is not taken into account.  $g(N = f, M = n)$  is the multiplicity

We begin the analysis by going back to the multiplying function for a single oscillator.

$$g(1,n) = 1 \quad \text{for all } n \text{ (or } s\text{)}.$$

We need a function to represent or generate the series

$$\sum_{n=0}^{\infty} g(1,n)t^n = \sum_{n=0}^{\infty} t^n = \frac{1}{1-t} \quad \text{for } |t| < 1.$$

For the problem of  $N$  oscillators, the generating function is

$$\left(\frac{1}{1-t}\right)^N = (1-t)^{-N} = \left(\sum_{n=0}^{\infty} t^n\right) = \sum_{n=0}^{\infty} g(N,n)t^n$$

because the number of ways a term  $t^n$  can appear in the  $N$ -fold product, is precisely the number of ordered ways in which the integer  $n$  can be formed as the sum of  $N$  non-negative integers.

$$\begin{aligned}\frac{d^n}{dt^n}(1-t)^{-N} &= \frac{d^{n-1}}{dt^{n-1}} N(1-t)^{-(N+1)} \\ &= N(N+1) \frac{d^{n-2}}{dt^{n-2}} (1-t)^{-(N+2)} \\ &= N(N+1)(N+2) \frac{d^{n-3}}{dt^{n-3}} (1-t)^{-(N+3)} \\ &= \dots\dots\dots \\ &= N(N+1)\dots(N+n-1)(1-t)^{-(N+n)} \\ &= \frac{(N+n-1)!}{(N-1)!} (1-t)^{-(N+n)}\end{aligned}$$

We have

$$g(N,n) = \lim_{t \rightarrow 0} \frac{1}{n!} \frac{d^n}{dt^n} (1-t)^{-N} = \frac{(N+n-1)!}{n!(N-1)!}$$

We use the Stirling's formula.

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

$$\begin{aligned}\ln g(N,n) &= \ln(N+n-1)! - \ln(n!) - \ln[(N-1)!] \\ &= (N-1) \ln\left(\frac{N+n-1}{N-1}\right) + n \ln\left(\frac{N+n-1}{n}\right) - \frac{1}{2} \ln(2\pi) \\ &\quad + \frac{1}{2} \ln\left(\frac{N+n-1}{n(N-1)}\right)\end{aligned}$$

or

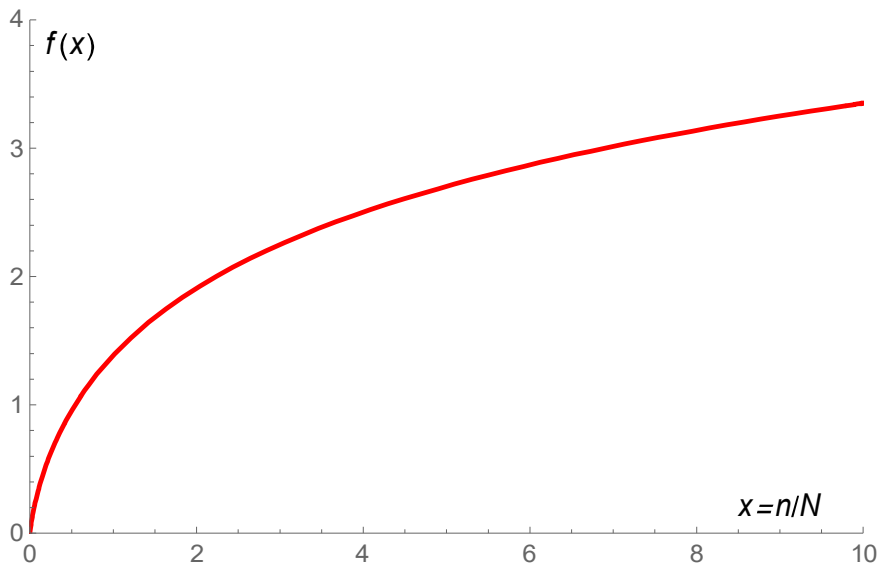
$$\begin{aligned}
\ln g(N, n) &\approx N \ln \left( \frac{N+n}{N} \right) + n \ln \left( \frac{N+n}{n} \right) + \frac{1}{2} \ln \left( \frac{N+n}{nN} \right) \\
&\approx N \ln \left( 1 + \frac{n}{N} \right) + n \ln \left( 1 + \frac{N}{n} \right) \\
&= N \left[ \ln \left( 1 + \frac{n}{N} \right) + \frac{n}{N} \ln \left( 1 + \frac{N}{n} \right) \right] \\
&= N \left[ \left( 1 + \frac{n}{N} \right) \ln \left( 1 + \frac{n}{N} \right) - \frac{n}{N} \ln \frac{n}{N} \right]
\end{aligned}$$

We make a plot of the function

$$f(x) = (1+x) \ln(1+x) - x \ln x$$

where

$$x = \frac{n}{N}$$



((**R. Kubo**)) R. Kubo, Statistical Mechanics (Elsevier Science, North-Holland, 1965) p.89  
Problem 26

## 5. ***N* independent oscillators**

The energy level of an oscillator with angular frequency  $\omega$  is given by

$$\varepsilon_s = (s + \frac{1}{2})\hbar\omega$$

with  $s = 0, 1, 2, \dots$ . When a system consisting of  $N$  almost independent oscillators, has the total energy

$$E = \frac{1}{2}N\hbar\omega + M\hbar\omega \quad (M; \text{integer})$$

(i) Find the thermodynamic weight  $W_M$ , and (ii) determine the relation between the temperature of this system and  $E$ .

**((Solution))**

If the quantum state of the  $i$ -th oscillator is given by  $|s_i\rangle$ , we have

$$E = \frac{1}{2}f\hbar\omega + M\hbar\omega = \frac{1}{2}f\hbar\omega + (s_1 + s_2 + \dots + s_f)\hbar\omega$$

or

$$s_1 + s_2 + \dots + s_f = n$$

Thus the thermodynamic weight  $W_n$  of a macroscopic state with the total energy  $E$  is equal to the number of ways of distributing  $n$  red balls among  $f$  labelled bars (|). A box may be empty since  $s_i = 0$  is possible. As is evident from **Fig.** one can get this number by finding the number of permutations of placing in a row all the red balls together with  $(f-1)$  that designate the dividing walls. For convenience, we use the black balls instead of the bar. If one labels all the balls with the running numbers,  $1, 2, 3, \dots, n+f-1$ , the number of permutations is  $(n+f-1)!$ . Note that the numbers of permutations among the balls with the same color are given by  $n!$  for red balls and  $(f-1)!$  for black balls. Thus we have

$$W_n = \frac{(f+n-1)!}{n!(f-1)!}$$

**((Example-1))**

$$f=5, \quad n=11.$$



$$s_1 + s_2 + s_3 + s_4 + s_5 = 2 + 5 + 0 + 3 + 1 = 11 = n$$

with

$$s_1 = 2 \quad |2\rangle$$

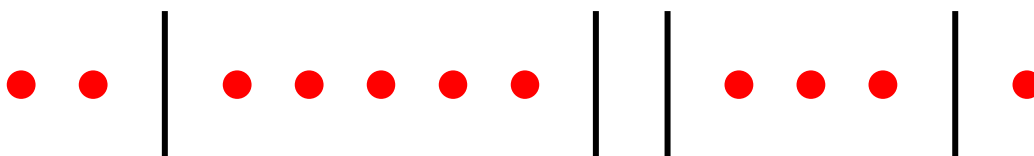
$$s_2 = 5 \quad |5\rangle$$

$$s_3 = 0 \quad |0\rangle$$

$$s_4 = 3 \quad |3\rangle$$

$$s_5 = 1 \quad |1\rangle$$

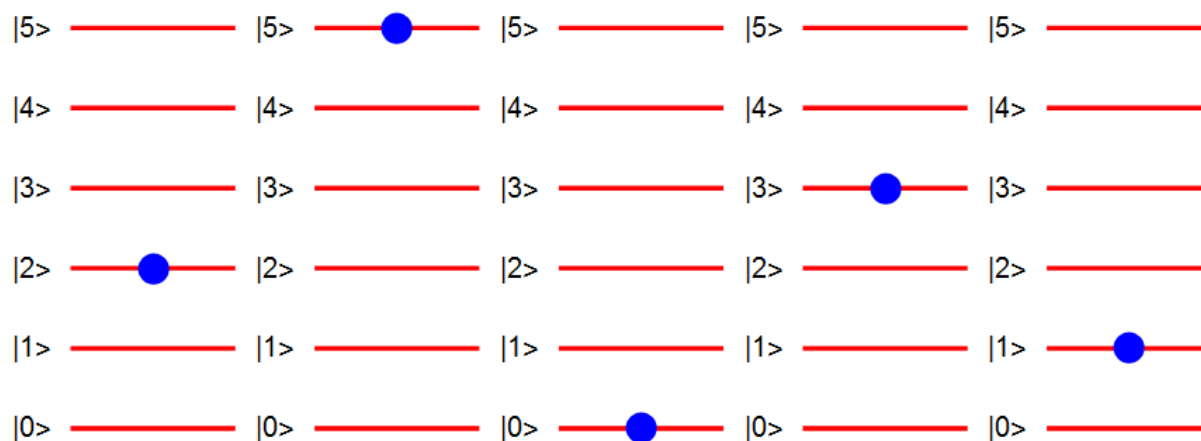
$$f - 1 = 4 \quad (\text{the number of walls}); \text{ the number of black dots}$$



which is equivalent to



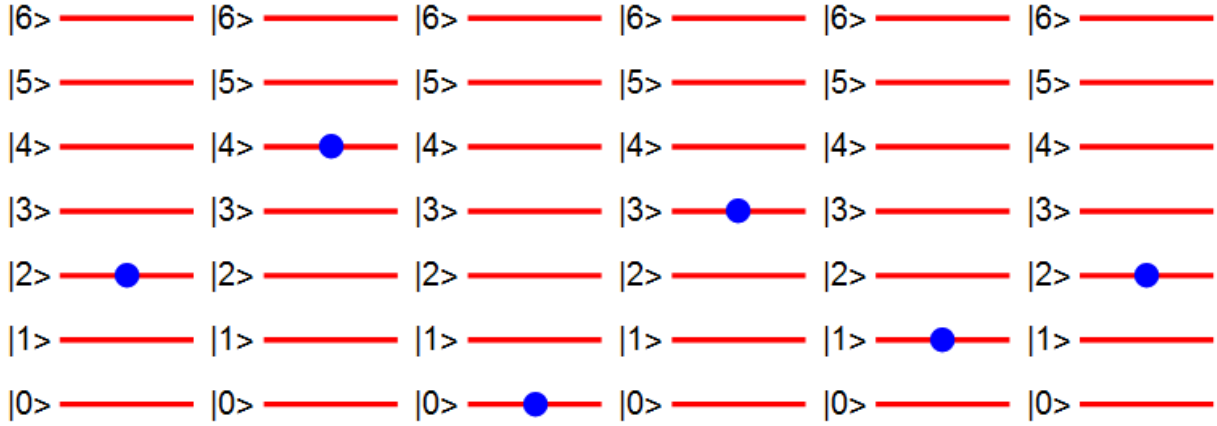
by replacing the bars by the black dots.



**((Example-2))**

$$f = 6, \quad n = 11.$$

$$s_1 + s_2 + s_3 + s_4 + s_5 + s_6 = 2 + 4 + 0 + 3 + 1 + 2 = 12 = n$$



There are 6 oscillators. The oscillator is in a state  $|s\rangle$ . The energy eigenvalue is  $(s + \frac{1}{2})\hbar\omega$ . In the above figure, we have one for  $|2\rangle$ , one for  $|4\rangle$ , one for  $|0\rangle$ , one for  $|3\rangle$ , one for  $|1\rangle$ , and one for one for  $|2\rangle$ . Then the total energy  $E$  is given by

$$\begin{aligned} E &= (2 + \frac{1}{2})\hbar\omega + (4 + \frac{1}{2})\hbar\omega + (0 + \frac{1}{2})\hbar\omega + (3 + \frac{1}{2})\hbar\omega + (1 + \frac{1}{2})\hbar\omega + (2 + \frac{1}{2})\hbar\omega \\ &= (2 + 4 + 0 + 3 + 1 + 2)\hbar\omega + \frac{6}{2}\hbar\omega \end{aligned}$$

where  $E = (n_1 + n_2 + \dots + n_f)\hbar\omega + \frac{f}{2}\hbar\omega = (n + \frac{f}{2})\hbar\omega$ , with  $n = n_1 + n_2 + \dots + n_f = 12$  and  $f = 6$ .

## 6. Microcanonical ensemble for the $f$ simple harmonics

We now calculate the entropy

$$\begin{aligned} S &= k_B \ln g(f, n) \\ &= f k_B \left[ \left(1 + \frac{n}{f}\right) \ln \left(1 + \frac{n}{f}\right) - \frac{n}{f} \ln \frac{n}{f} \right] \\ &= f k_B \left[ \left(\frac{1}{2} + \frac{E}{f\hbar\omega}\right) \ln \left(\frac{1}{2} + \frac{E}{f\hbar\omega}\right) - \left(\frac{E}{f\hbar\omega} - \frac{1}{2}\right) \ln \left(\frac{E}{f\hbar\omega} - \frac{1}{2}\right) \right] \end{aligned}$$

where

$$\frac{n}{f} = \frac{E}{f\hbar\omega} - \frac{1}{2}$$

The temperature  $T$  is defined as

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_V = \frac{k_B}{\hbar\omega} \ln \left( \frac{\frac{E}{f\hbar\omega} + \frac{1}{2}}{\frac{E}{f\hbar\omega} - \frac{1}{2}} \right)$$

or

$$\exp\left(\frac{\hbar\omega}{k_B T}\right) = \frac{\frac{E}{f\hbar\omega} + \frac{1}{2}}{\frac{E}{f\hbar\omega} - \frac{1}{2}} = 1 + \frac{1}{\frac{E}{f\hbar\omega} - \frac{1}{2}}$$

or

$$\frac{E}{f} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

## 7. Canonical ensemble

The partition function for one harmonics

$$\begin{aligned} Z_{C1} &= \sum_{n=0}^{\infty} \exp[-\beta(n + \frac{1}{2})\hbar\omega] \\ &= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \\ &= \frac{e^{\beta\hbar\omega/2}}{e^{\beta\hbar\omega} - 1} \end{aligned}$$

The partitions function for  $f$  simple harmonics

$$Z_{CN}(\beta) = (Z_{C1})^f \\ = e^{-f\beta\hbar\omega/2} (1 - e^{-\beta\hbar\omega})^{-f}$$

$$Z_{CN}(\beta) = \int dE \Omega(E) \exp(-\beta E) \quad (\text{Laplace transformation})$$

The inverse Laplace transformation

$$\Omega(E) = \frac{1}{2\pi i} \int d\beta Z_{CN}(\beta) e^{\beta E} \\ = \frac{1}{2\pi i} \int d\beta e^{\beta(E - \frac{f\hbar\omega}{2})} (1 - e^{-\beta\hbar\omega})^{-f}$$

Note that

$$(1-t)^{-f} = \sum_{n=0}^{\infty} \frac{(f+n-1)}{(f-1)!n!} t^n$$

Then we have the density of states as

$$\Omega(E) = \sum_{n=0}^{\infty} \frac{(f+n-1)}{(f-1)!n!} \frac{1}{2\pi i} \int d\beta e^{\beta(E - \frac{f\hbar\omega}{2} - n\hbar\omega)}$$

When  $\beta = ix$ ,

$$\Omega(E) = \sum_{n=0}^{\infty} \frac{(f+n-1)}{(f-1)!n!} \frac{1}{2\pi} \int dx \beta e^{ix(E - \frac{f\hbar\omega}{2} - n\hbar\omega)} \\ = \sum_{n=0}^{\infty} \frac{(f+n-1)}{(f-1)!n!} \delta(E - \frac{f\hbar\omega}{2} - n\hbar\omega)$$

## 8. Canonical ensemble for the $f$ - simple harmonics

The one-oscillator partition function is given by

$$Z_{C1} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = e^{-\frac{\beta\hbar\omega}{2}} \frac{1}{1 - e^{-\beta\hbar\omega}}$$

The  $f$ -oscillator partition function is given by

$$(Z_{cf})^f = e^{-\frac{\beta \hbar \omega}{2}} \left( \frac{1}{1 - e^{-\beta \hbar \omega}} \right)^f$$

when  $x = e^{-\beta \hbar \omega}$ . The partition function for the  $f$ -harmonic oscillators can be rewritten as

$$\begin{aligned} Z_{cf} &= e^{-\frac{\beta \hbar \omega}{2}} \left( \frac{1}{1 - x} \right)^f \\ &= e^{-\frac{\beta \hbar \omega}{2}} (1 - e^{-\beta \hbar \omega})^{-f} \\ &= e^{-\frac{\beta \hbar \omega}{2}} \sum_{m=0}^{\infty} \frac{(f-1+m)!}{(f-1)!m!} e^{-m\beta \hbar \omega} \\ &= \sum_{m=0}^{\infty} \frac{(f-1+m)!}{(f-1)!m!} e^{-\frac{\beta \hbar \omega}{2}} e^{-m\beta \hbar \omega} \end{aligned}$$

where

$$\left( \frac{1}{1-x} \right)^f = \sum_{m=0}^{\infty} \frac{(f-1+m)!}{(f-1)!m!} x^m \quad (\text{see the proof using Mathematica below}).$$

The multiplicity (degeneracy) for the  $|E_m\rangle$  state is

$$g(f, m) = \frac{(f-1+m)!}{(f-1)!m!}$$

and the energy for the  $|E_m\rangle$  state is given by

$$E_m = m\hbar\omega + \frac{1}{2}f\hbar\omega = \left(m + \frac{f}{2}\right)\hbar\omega.$$

where  $\frac{1}{2}f\hbar\omega$  is the zero point energy.

**((Mathematica))**

```
Clear["Global`*"]; g[f_, m_] := 
$$\frac{(f + m - 1)!}{(f - 1)! m!};$$

```

```
eq1 = Series[
$$\left(\frac{1}{1 - x}\right)^{15}, \{x, 0, 20\}]$$

```

```
1 + 15 x + 120 x2 + 680 x3 + 3060 x4 + 11 628 x5 +
  38 760 x6 + 116 280 x7 + 319 770 x8 + 817 190 x9 +
  1 961 256 x10 + 4 457 400 x11 + 9 657 700 x12 +
  20 058 300 x13 + 40 116 600 x14 + 77 558 760 x15 +
  145 422 675 x16 + 265 182 525 x17 + 471 435 600 x18 +
  818 809 200 x19 + 1 391 975 640 x20 + O[x]21
```

```
A1[n_] := Coefficient[eq1, x, n];
```

```
list1 = Table[{n, g[15, n], A1[n]}, {n, 0, 20}];
```

```
Prepend[Table[{n, g[15, n], A1[n]}, {n, 0, 20}],
  {"n", " g[f=15,n]", "coefficient(xn)"}] //
TableForm
```

n	g[f=15,n]	coefficient( $x^n$ )
0	1	1
1	15	15
2	120	120
3	680	680
4	3060	3060
5	11 628	11 628
6	38 760	38 760
7	116 280	116 280
8	319 770	319 770
9	817 190	817 190
10	1 961 256	1 961 256
11	4 457 400	4 457 400
12	9 657 700	9 657 700
13	20 058 300	20 058 300
14	40 116 600	40 116 600
15	77 558 760	77 558 760
16	145 422 675	145 422 675
17	265 182 525	265 182 525
18	471 435 600	471 435 600
19	818 809 200	818 809 200
20	1 391 975 640	1 391 975 640