CHAPTER 13

THERMAL PROPERTIES OF HARMONIC OSCILLATORS

INTRODUCTION

Using the concepts encountered in the previous chapter, Chapter 13 is concerned with the thermal properties of oscillators and specially by thermal average energies, heat capacities, thermal fluctuations of energy, position, and momentum and thermal entropies. It ends by giving the detailed demonstration of the thermal average over Boltzmann density operators for harmonic oscillator, of very general functions of Boson operators, which admits as a special case the *Bloch's theorem* dealing with the thermal average of the *translation operator*.

13.1 BOLTZMANN DISTRIBUTION LAW INSIDE A LARGE POPULATION OF EQUIVALENT OSCILLATORS

Consider a set of N equivalent quantum harmonic oscillators with the same Hamiltonian

$$\mathbf{H}_k = \hbar\omega\left(\mathbf{a}_k^\dagger \mathbf{a}_k + \frac{1}{2}\right)$$

In the following we shall suppose that N is very large, its magnitude being, for instance, Avogadro's number. The eigenvalue equation of these Hamiltonians $\mathbf{H}_k$ is

$$\mathbf{H}_k|\{n\}_k\rangle = E_k^\circ|\{n\}_k\rangle$$

with, neglecting the same zero-point energies,

$$E_k^\circ = n_k\hbar\omega \tag{13.1}$$

Now, assume that this set of oscillators cannot exchange energy with the neigborhood, so that the total energy E_{Tot} of the set is constant and suppose that each oscillator may exchange energy with the other ones.

In any configuration, among a multitude, the total energy E_{Tot} of the set is

$$E_{\mathrm{Tot}} = \sum_k E_k^\circ N_k \tag{13.2}$$

Quantum Oscillators, First Edition. Olivier Henri-Rousseau and Paul Blaise.

where N_k is the number of oscillators having the same eigenvalue energy E_k° defined by Eq. (13.1). Of course, the total number N of oscillators is the sum over the numbers N_k , that is,

$$N_{\text{Tot}} = \sum_k N_k \tag{13.3}$$

Since the number of oscillators and the total energy are constant, one has, respectively,

$$dE_{\text{Tot}} = 0 \qquad \text{and} \qquad dN_{\text{Tot}} = 0$$

Thus, Eqs. (13.2) and (13.3) lead to

$$\sum_k E_k^\circ dN_k = 0 \qquad \text{and} \qquad \sum_k dN_k = 0 \tag{13.4}$$

The statistical weight of a configuration corresponding to a situation where there are N_1 oscillators having the energy E_1, N_2 oscillators having the energy E_2, and so on is given by the statistical distribution

$$W(N_1, N_2, \ldots) = \frac{N_{\text{Tot}}!}{\prod_k N_k!} \tag{13.5}$$

where the N_k are constrained to verify simultaneously Eqs. (13.4).

Figure 13.1 gives for a set of $N_{\text{Tot}} = 21$ oscillators, the values of $W(N_1, N_2, \ldots)$ calculated by Eq. (13.5), subjected to the constraints of Eqs. (13.4), when applied to eight possible distributions of the total energy $E_{\text{Tot}} = 21\hbar\omega$.

Inspection of Fig. 13.1 shows that some configurations are more probable than others. The most probable is that corresponding to the situation where there are less and less oscillators when the energy increases.

We shall now show that the most probable configuration is that corresponding to the situation where the number of oscillators having a given energy is exponentially decreasing with energy. Thus, we write Eq. (13.5) in logarithm form, that is,

$$\ln W(N_1, N_2, \ldots) = \ln (N_{\text{Tot}}!) - \sum_k \ln (N_k!) \tag{13.6}$$

Now, in order to find the most probable configurations, the differential of Eq. (13.6) must be zero, that is,

$$d \ln W(N_1, N_2, \ldots) = -\sum_k \left(\frac{\partial \ln (N_k!)}{\partial N_k} \right) dN_k = 0 \tag{13.7}$$

Next, in order to take into account the two constraints (13.4) on the $N_k{}^{\text{eq}}$, one must use the Lagrange multipliers method described in Section 18.7 leading one to write in place of Eq. (13.7) the following equation:

$$-\sum_k \left(\frac{\partial \ln (N_k{}^{\text{eq}}!)}{\partial N_k{}^{\text{eq}}} \right) dN_k{}^{\text{eq}} - \beta \sum_k E_k \, dN_k{}^{\text{eq}} + \alpha \sum_k dN_k{}^{\text{eq}} = 0$$

Since this last expression must hold for each k, we see that they are as many following equations as they are of k:

$$-\left\{ \left(\frac{\partial \ln (N_k{}^{\text{eq}}!)}{\partial N_k{}^{\text{eq}}} \right) + \beta E_k - \alpha \right\} dN_k{}^{\text{eq}} = 0 \tag{13.8}$$

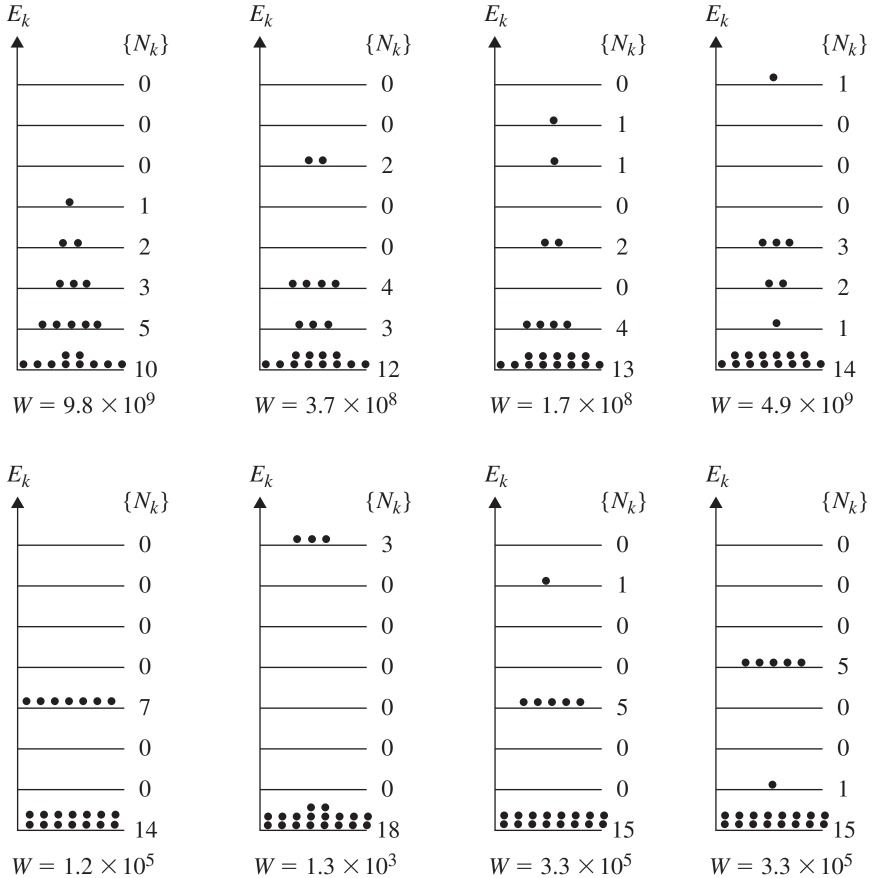

Figure 13.1 Values of $W(N_1, N_2, \ldots)$ calculated by Eqs. (13.5) and for $N_{\text{Tot}} = 21$, $E_{\text{Tot}} = 21\hbar\omega$, for eight different configurations verifying Eqs. (13.4). For each configuration, the eight lowest energy levels E_k of the quantum harmonic oscillators are reproduced, with for each of them, as many dark circles as they are (N_k) of oscillators having the corresponding energy E_k.

In order to calculate the partial derivative of Eq. (13.6) with respect to ${N_k}^{\text{eq}}$, it is convenient, if the numbers N and ${N_k}^{\text{eq}}$ are very large, to use the Stirling approximation

$$\ln({N_k}^{\text{eq}}!) \backsimeq {N_k}^{\text{eq}} \ln({N_k}^{\text{eq}}) - {N_k}^{\text{eq}}$$

Then, the partial derivative of Eq. (13.6) of interest reads

$$\left(\frac{\partial \ln({N_k}^{\text{eq}}!)}{\partial {N_k}^{\text{eq}}}\right) \backsimeq \ln({N_k}^{\text{eq}})$$

Hence, Eq. (13.8) is

$$(-\ln {N_k}^{\text{eq}} - \beta E_k + \alpha) d{N_k}^{\text{eq}} = 0$$

Moreover, since $d{N_k}^{\text{eq}} \neq 0$, it yields

$$-\ln {N_k}^{\text{eq}} - \beta E_k + \alpha = 0$$

so that

$$N_k{}^{\text{eq}} = e^{\alpha} e^{-\beta E_k} \tag{13.9}$$

It is this distribution that is the closest to the one described by the configuration of Fig. 13.1 corresponding to the situation leading to $W = 9.8 \times 10^9$ and where $N_0 = 10$ for $E_0 = 0, N_1 = 5$ for $E_1 = 1, N_2 = 3$ for $E_2 = 2, N_3 = 2$ for $E_3 = 3, N_4 = 1$ for $E_4 = 4$, and $N_k = 0$ for the higher levels.

The expression for the Lagrange multiplier α may be obtained by aid of Eqs. (13.3) and (13.9) yielding

$$N_{\text{Tot}} = e^{\alpha} \sum_k e^{-\beta E_k}$$

so that

$$e^{\alpha} = \frac{N_{\text{Tot}}}{Z} \tag{13.10}$$

where Z is the partition function:

$$Z = \sum_k e^{-\beta E_k}$$

As a consequence, the Lagrange parameter α appears to be

$$\alpha = \ln\left(\frac{N_{\text{Tot}}}{Z}\right)$$

Moreover, with the help of Eq. (13.10), Eq. (13.9) becomes

$$N_k{}^{\text{eq}} = \frac{N_{\text{Tot}}}{Z} e^{-\beta E_k}$$

or

$$N_k{}^{\text{eq}} = N_{\text{Tot}} W^{\text{eq}}(E_k)$$

where $W^{\text{eq}}(E_k)$ is the Boltzmann probability to find oscillators having the energy E_k, which is given by

$$\boxed{W^{\text{eq}}(E_k) = \frac{e^{-\beta E_k}}{Z}} \tag{13.11}$$

Recall that the value of the Lagrange parameter β appearing in the exponential and decreasing with the energy levels E_k has been found above to be given by Eq. (12.90).

13.2 THERMAL PROPERTIES OF HARMONIC OSCILLATORS

13.2.1 Canonical density operators of harmonic oscillators

Consider the canonical density operator $\boldsymbol{\rho}_B$ of a quantum harmonic oscillator defined by Eq. (12.61), that is,

$$\boldsymbol{\rho}_B = \frac{1}{Z}(e^{-\beta \mathbf{H}}) \tag{13.12}$$

where Z is the partition function given by Eq. (12.62), that is,

$$Z = \mathbf{tr}\{(e^{-\beta\mathbf{H}})\} \tag{13.13}$$

β is the thermal Lagrange parameter given by Eq. (12.90), that is,

$$\beta = \frac{1}{k_B T} \tag{13.14}$$

and $\mathbf{H}$ is the Hamiltonian of the harmonic oscillator given by Eq. (5.9), that is,

$$\mathbf{H} = \hbar\omega\left(\mathbf{a}^\dagger\mathbf{a} + \tfrac{1}{2}\right) \quad \text{with} \quad [\mathbf{a}, \mathbf{a}^\dagger] = 1 \tag{13.15}$$

Owing to Eqs. (13.12) and (13.15), the canonical density operator of the harmonic oscillator reads

$$\boldsymbol{\rho}_B = \frac{1}{Z}(e^{-\beta\mathbf{a}^\dagger\mathbf{a}\hbar\omega}e^{-\beta\hbar\omega/2}) \tag{13.16}$$

so that the partition function (13.13) yields

$$Z = (e^{-\beta\hbar\omega/2})\mathbf{tr}\{(e^{-\beta\mathbf{a}^\dagger\mathbf{a}\hbar\omega})\} \tag{13.17}$$

Now, to perform the trace involved in this last equation, it is convenient to use the basis of eigenstates of $\mathbf{a}^\dagger\mathbf{a}$, that is,

$$\mathbf{a}^\dagger\mathbf{a}|(n)\rangle = n|(n)\rangle \quad \text{with} \quad \langle(n)|(m)\rangle = \delta_{nm} \tag{13.18}$$

Hence, owing to Eq. (13.15), the partition function (13.13) takes the form

$$Z = (e^{-\beta\hbar\omega/2})\sum_n \langle(n)|(e^{-\beta\mathbf{a}^\dagger\mathbf{a}\hbar\omega})|(n)\rangle$$

Expanding the exponential operator gives

$$Z = (e^{-\beta\hbar\omega/2})\sum_n\sum_k \langle(n)|\left(\frac{(-\beta\hbar\omega)^k(\mathbf{a}^\dagger\mathbf{a})^k}{k!}\right)|(n)\rangle \tag{13.19}$$

Moreover, due to Eq. (13.18) one obtains by recurrence

$$(\mathbf{a}^\dagger\mathbf{a})^k|(n)\rangle = n^k|(n)\rangle$$

so that Eq. (13.19) transforms to

$$Z = (e^{-\beta\hbar\omega/2})\sum_n\sum_k \langle(n)|\left(\frac{(-\beta\hbar\omega)^k n^k}{k!}\right)|(n)\rangle$$

Hence, after coming back to the exponential

$$Z = (e^{-\beta\hbar\omega/2})\sum_n \langle(n)|(e^{-\beta n\hbar\omega})|(n)\rangle$$

and using the normality property of the kets

$$Z = (e^{-\beta\hbar\omega/2})\sum_n (e^{-\beta n\hbar\omega})$$

we have

$$Z = (e^{-\beta\hbar\omega/2}) \sum_n y^n \quad \text{with} \quad y = (e^{-\beta\hbar\omega}) \tag{13.20}$$

Now, observe that at temperatures T, which are not very far from the room temperature, the following inequality is generally satisfied for harmonic oscillators describing molecular vibrations:

$$\hbar\omega > k_B T$$

so that, due to Eq. (13.14),

$$\beta\hbar\omega > 1 \qquad \text{and thus} \qquad e^{-\beta\hbar\omega} < 1$$

In this special situation, the series involved in Eq. (13.20) is convergent and given by

$$\sum_n y^n = \frac{1}{1-y} \quad \text{with} \quad y < 1$$

Hence, the partition function (13.20) becomes

$$Z = \left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}\right) = \left(\frac{e^{-\hbar\omega/2k_BT}}{1 - e^{-\hbar\omega/k_BT}}\right) \tag{13.21}$$

a result that may also be written

$$Z = \left(\frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}}\right) = \frac{1}{2\sinh(\hbar\omega/2)}$$

Moreover, the canonical density operator (13.16) becomes after simplification

$$\boldsymbol{\rho}_B = (1 - e^{-\beta\hbar\omega})(e^{-\beta\mathbf{a}^\dagger\mathbf{a}\hbar\omega}) \tag{13.22}$$

a result that may be also written

$$\boxed{\boldsymbol{\rho}_B = (1 - e^{-\lambda})(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})} \tag{13.23}$$

and, comparing Eq. (13.14),

$$\boxed{\lambda = \frac{\hbar\omega}{k_BT} = \beta\hbar\omega} \tag{13.24}$$

13.2.2 Thermal energy

Now, consider the mean thermal average energy of a quantum harmonic oscillator that is the average of the Hamiltonian over the canonical density operator, that is,

$$\langle\mathbf{H}\rangle = \mathbf{tr}\{\boldsymbol{\rho}_B\mathbf{H}\} \tag{13.25}$$

which, due to Eqs. (13.12) and (13.23), reads either

$$\langle\mathbf{H}\rangle = \hbar\omega(1 - e^{-\lambda})\,\mathbf{tr}\left\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\left(\mathbf{a}^\dagger\mathbf{a} + \tfrac{1}{2}\right)\right\} \tag{13.26}$$

or, due to Eq. (13.22),

$$\langle\mathbf{H}\rangle = \hbar\omega(1 - e^{-\beta\hbar\omega})\,\mathbf{tr}\{(e^{-\beta\mathbf{a}^\dagger\mathbf{a}\hbar\omega})\mathbf{a}^\dagger\mathbf{a}\} + \frac{\hbar\omega}{2} \tag{13.27}$$

However, observe it is unnecessary to separately calculate the partition function and the trace involved in Eq. (13.27), since it has been shown that the thermal average energy (13.25) of a system whatever its Hamiltonian may be, is given by Eq. (12.69), that is,

$$\langle \mathbf{H} \rangle = -\left(\frac{\partial \ln Z}{\partial \beta} \right) \tag{13.28}$$

so that it is possible to get the thermal average value of the energy (13.25) using Eq. (13.28). Hence, start from Eq. (13.21) giving $\ln Z$, that is,

$$\ln (Z) = -\beta \frac{\hbar\omega}{2} - \ln (1 - e^{-\beta\hbar\omega})$$

so that, by differentiation, one obtains

$$\left(\frac{\partial \ln Z}{\partial \beta} \right) = -\frac{\hbar\omega}{2} - \left(\frac{\hbar\omega \, e^{-\beta\hbar\omega}}{1 - \, e^{-\beta\hbar\omega}} \right)$$

or, after rearranging,

$$\left(\frac{\partial \ln Z}{\partial \beta} \right) = -\left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} + \frac{\hbar\omega}{2} \right)$$

Thus, comparing Eq. (13.14), the thermal average energy (13.28) becomes

$$\boxed{\langle \mathbf{H} \rangle = \left(\frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} + \frac{\hbar\omega}{2} \right)} \tag{13.29}$$

which is the Planck expression of the average energy of a quantum oscillator belonging to a population of quantum harmonic oscillators in thermal equilibrium. Of course, the total average energy of a population of N oscillators is

$$\langle \mathbf{H}_{\mathrm{Tot}} \rangle = N \, \langle \mathbf{H} \rangle \tag{13.30}$$

Moreover, by comparison of Eqs. (13.27) and (13.29), it yields

$$(1 - e^{-\beta\hbar\omega})\mathbf{tr}\{(e^{-\beta\hbar\omega\mathbf{a}^\dagger\mathbf{a}})\mathbf{a}^\dagger\mathbf{a}\} = \frac{1}{e^{\beta\hbar\omega} - 1} \tag{13.31}$$

or

$$(1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\mathbf{a}^\dagger\mathbf{a}\ \} = \frac{1}{e^{\lambda} - 1} \tag{13.32}$$

13.2.3 Boltzmann distribution

Now, consider the diagonal matrix elements of the density operator as given by Eq. (12.85), that is,

$$P_n = \langle (n) | \boldsymbol{\rho}_B | (n) \rangle \tag{13.33}$$

Then, comparing Eq. (13.12), the right-hand-side matrix elements read

$$\langle (n) | \boldsymbol{\rho}_B | (n) \rangle = \frac{1}{Z} \langle (n) | (e^{-\beta\mathbf{H}}) | (n) \rangle$$

or, due to Eq. (13.22),

$$\langle (n)|\boldsymbol{\rho}_B|(n)\rangle = (1 - e^{-\beta\hbar\omega})\langle (n)|(e^{-\beta\hbar\omega \mathbf{a}^\dagger \mathbf{a}})|(n)\rangle$$

Hence, after using the eigenvalue equation

$$\mathbf{a}^\dagger \mathbf{a}|(n)\rangle = n|(n)\rangle$$

the matrix elements become

$$\langle (n)|\boldsymbol{\rho}_B|(n)\rangle = (1 - e^{-\beta\hbar\omega})\langle (n)|e^{-n\beta\hbar\omega}|(n)\rangle$$

or

$$\langle (n)|\boldsymbol{\rho}_B|(n)\rangle = (1 - e^{-\beta\hbar\omega})(e^{-n\beta\hbar\omega})$$

Hence, Eq. (13.33) yields

$$\boxed{P_n = (1 - e^{-\beta\hbar\omega})(e^{-n\beta\hbar\omega})} \tag{13.34}$$

This last result, which is the Boltzmann distribution of the energy level of harmonic oscillators, that is, the probability for them to be occupied at any temperature, may be put in correspondence with the result (12.28) obtained in the coarse-grained analysis where an exponential decreasing with energy of the probability occupation appears.

13.2.4 Thermal average of the occupation number

Now, observe that, due to Eq. (13.31), and since the occupation number is defined by

$$\mathbf{n} \equiv \mathbf{a}^\dagger \mathbf{a} \tag{13.35}$$

it appears that its thermal average is

$$\langle \mathbf{n} \rangle = \frac{1}{e^{\beta\hbar\omega} - 1} \tag{13.36}$$

Next, comparing Eq. (13.36),

$$1 + \langle \mathbf{n} \rangle = 1 + \frac{1}{e^{\beta\hbar\omega} - 1} = \frac{e^{\beta\hbar\omega}}{e^{\beta\hbar\omega} - 1}$$

the ratio of $\langle \mathbf{n} \rangle$ and $1 + \langle \mathbf{n} \rangle$ yields

$$\frac{\langle \mathbf{n} \rangle}{1 + \langle \mathbf{n} \rangle} = e^{-\beta\hbar\omega} \tag{13.37}$$

Besides, from Eq. (13.37) it reads

$$(1 - e^{-\beta\hbar\omega}) = 1 - \frac{\langle \mathbf{n} \rangle}{1 + \langle \mathbf{n} \rangle} = \frac{1}{1 + \langle \mathbf{n} \rangle} \tag{13.38}$$

while the *nth* power of (13.37) takes the form

$$(e^{-n\beta\hbar\omega}) = \left(\frac{\langle \mathbf{n} \rangle}{1 + \langle \mathbf{n} \rangle} \right)^n \tag{13.39}$$

so that it results from Eqs. (13.39) and (13.38) that

$$(1 - e^{-\beta\hbar\omega})(e^{-n\beta\hbar\omega}) = \frac{1}{1 + \langle \mathbf{n} \rangle} \left(\frac{\langle \mathbf{n} \rangle}{1 + \langle \mathbf{n} \rangle} \right)^n$$

Hence, the Boltzmann distribution function (13.34) becomes

$$\boxed{P_n = \frac{\langle \mathbf{n} \rangle^n}{(1 + \langle \mathbf{n} \rangle)^{n+1}}} \tag{13.40}$$

a result that is widely used in the area of the theory of lasers.

13.2.5 Heat capacity

Now, consider the thermal capacity at constant volume C_v which is, by definition, the time derivative of the total average energy of a population of N oscillators:

$$C_v = \left(\frac{\partial \langle \mathbf{H}_{\text{Tot}}(T) \rangle}{\partial T} \right)_v \tag{13.41}$$

where $\mathbf{H}_{\text{Tot}}$ is given by Eq. (13.30) so that

$$C_v = N \left(\frac{\partial \langle \mathbf{H}(T) \rangle}{\partial T} \right)_v$$

Then, due to Eq. (13.29), Eq. (13.41) reads

$$C_v = N\hbar\omega \frac{\partial}{\partial T} \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} \right)$$

and thus, on differentiation

$$C_v = N\hbar\omega \left(\frac{-1}{(e^{\hbar\omega/k_B T} - 1)^2} \right) e^{\hbar\omega/k_B T} \left(\frac{-\hbar\omega}{k_B T^2} \right)$$

or

$$C_v = N k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \tag{13.42}$$

Figure 13.2 discusses the evolution with temperature of the thermal capacity C_v for a mole of oscillators of angular frequency $\omega = 1000\,\text{cm}^{-1}$.

13.2.6 Thermal fluctuations

13.2.6.1 Thermal energy fluctuation Now, the thermal fluctuation of the energy of N oscillators is

$$\Delta E_{\text{Tot}} = \sqrt{\langle \mathbf{H}_{\text{Tot}}{}^2 \rangle - \langle \mathbf{H}_{\text{Tot}} \rangle^2} \tag{13.43}$$

with

$$\langle \mathbf{H}_{\text{Tot}}{}^2 \rangle = N^2 \langle \mathbf{H}^2 \rangle$$

Thus Eq. (13.30), becomes

$$\Delta E_{\text{Tot}} = N\sqrt{\langle \mathbf{H}^2 \rangle - \langle \mathbf{H} \rangle^2}$$

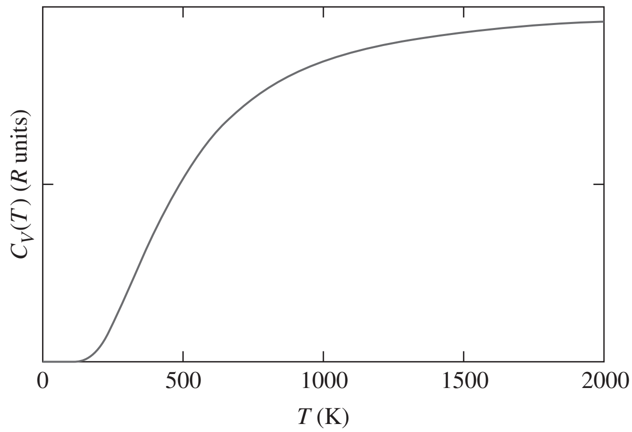

Figure 13.2 Thermal capacity C_v in R units for a mole of oscillators of angular frequency $\omega = 1000\,\text{cm}^{-1}$.

Recall that the thermal average of the Hamiltonian may be obtained by Eq. (12.69), that is,

$$\langle \mathbf{H} \rangle = -\left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \tag{13.44}$$

Now, the thermal average of $\mathbf{H}^2$ may be found from

$$\langle \mathbf{H}^2 \rangle = \mathbf{tr}\{\boldsymbol{\rho}_B \mathbf{H}^2\}$$

so that, due to Eq. (13.12), we have

$$\langle \mathbf{H}^2 \rangle = \frac{1}{Z} \mathbf{tr}\{(e^{-\beta \mathbf{H}}) \mathbf{H}^2\} \tag{13.45}$$

Next, observe that the product of operators appearing under the trace may be written

$$(e^{-\beta \mathbf{H}}) \mathbf{H}^2 = \left(\frac{\partial^2 e^{-\beta \mathbf{H}}}{\partial \beta^2} \right) \tag{13.46}$$

so that Eq. (13.45) reads

$$\langle \mathbf{H}^2 \rangle = \frac{1}{Z} \mathbf{tr} \left\{ \left(\frac{\partial^2}{\partial \beta^2} \right) \left(e^{-\beta \mathbf{H}} \right) \right\}$$

or, since the partial derivative commutes with the trace operation,

$$\langle \mathbf{H}^2 \rangle = \frac{1}{Z} \left(\frac{\partial^2}{\partial \beta^2} \right) \mathbf{tr}\{(e^{-\beta \mathbf{H}})\} \tag{13.47}$$

Again, since the partition function is given by Eqs. (13.13) and (13.14), that is,

$$Z = \mathbf{tr}\{(e^{-\beta \mathbf{H}})\} \quad \text{and} \qquad \beta = \frac{1}{k_B T} \tag{13.48}$$

Eq. (13.47) reads

$$\langle \mathbf{H}^2 \rangle = \left\{ \frac{1}{Z} \left(\frac{\partial^2 Z}{\partial \beta^2} \right) \right\} \tag{13.49}$$

Now, observe that the following equation is satisfied:

$$\left(\frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)\right) = \left(\frac{\partial}{\partial\beta}\frac{1}{Z}\right)\left(\frac{\partial Z}{\partial\beta}\right) + \left\{\frac{1}{Z}\left(\frac{\partial^2 Z}{\partial\beta^2}\right)\right\}$$

which yields

$$\left(\frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)\right) = -\frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)\left(\frac{\partial Z}{\partial\beta}\right) + \left\{\frac{1}{Z}\left(\frac{\partial^2 Z}{\partial\beta^2}\right)\right\}$$

Hence, equating the last right-hand side of this last equation and the right-hand side of Eq. (13.49) leads to

$$\langle\mathbf{H}^2\rangle = \left(\frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)\right) + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2$$

or, because of Eq. (13.44), to

$$\langle\mathbf{H}^2\rangle = -\left(\frac{\partial\langle\mathbf{H}\rangle}{\partial\beta}\right) + \langle\mathbf{H}\rangle^2 \tag{13.50}$$

Hence, the thermal energy fluctuation (13.43) is

$$\Delta E_{\text{Tot}} = N\sqrt{-\left(\frac{\partial\langle\mathbf{H}\rangle}{\partial\beta}\right)}$$

or

$$\Delta E_{\text{Tot}} = N\sqrt{-\left(\frac{\partial\langle\mathbf{H}\rangle}{\partial T}\right)\left(\frac{\partial T}{\partial\beta}\right)}$$

and thus, due to the definition (13.41) of the heat capacity at constant volume C_v,

$$\Delta E_{\text{Tot}} = N\sqrt{-\frac{C_v}{N}\left(\frac{\partial T}{\partial\beta}\right)} \tag{13.51}$$

Again, owing to Eq. (13.14) leading to

$$T = \frac{1}{k_B\beta} \tag{13.52}$$

the partial derivative of the absolute temperature with respect to β reads

$$\left(\frac{\partial T}{\partial\beta}\right) = \frac{\partial}{\partial\beta}\left(\frac{1}{k_B\beta}\right) = -\left(\frac{1}{k_B\beta^2}\right)$$

and thus, thanks to (13.52),

$$\left(\frac{\partial T}{\partial\beta}\right) = -k_B T^2$$

Thus, owing to this result, and to the expression (13.42) for the heat capacity, Eq. (13.51) leads to

$$\Delta E_{\text{Tot}} = \sqrt{N}\sqrt{k_B\left(\frac{\hbar\omega}{k_B T}\right)^2\frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T}-1)^2}k_B T^2}$$

or, after simplification,

$$\Delta E_{\mathrm{Tot}} = \sqrt{N}\hbar\omega \frac{e^{\hbar\omega/2k_BT}}{(e^{\hbar\omega/k_BT} - 1)}$$

Besides, keeping in mind that, due to Eq. (13.29), and when the zero-point energy is ignored, the thermal average (13.30) reduces to

$$\langle \mathbf{H}_{\mathrm{Tot}} \rangle = N \frac{\hbar\omega}{(e^{\hbar\omega/k_BT} - 1)}$$

the relative energy fluctuation becomes

$$\frac{\Delta E_{\mathrm{Tot}}}{\langle \mathbf{H}_{\mathrm{Tot}} \rangle} = \frac{1}{\sqrt{N}} e^{\hbar\omega/2k_BT}$$

At high temperature, the argument of the exponential being very small, the relative fluctuation reduces to

$$\frac{\Delta E_{\mathrm{Tot}}}{\langle \mathbf{H}_{\mathrm{Tot}} \rangle} \to \frac{1}{\sqrt{N}}$$

It must be emphasized that the inverse dependence of the relative fluctuation with respect to the number N of oscillators is the same as that of (12.39) yet encountered in the previous section, dealing with a coarse-grained analysis of a large set of coupled harmonic oscillators.

13.2.6.2 Thermal number occupation fluctuation Starting from Eq. (13.50), that is,

$$\langle \mathbf{H}^2 \rangle = -\left(\frac{\partial \langle \mathbf{H} \rangle}{\partial \beta} \right) + \langle \mathbf{H} \rangle^2 \tag{13.53}$$

and passing to Boson operators using Eq. (5.9), reads

$$\left\langle \left(\mathbf{a}^\dagger \mathbf{a} + \frac{1}{2} \right)^2 \right\rangle = -\frac{1}{\hbar\omega} \left(\frac{\partial \langle (\mathbf{a}^\dagger \mathbf{a} + \frac{1}{2}) \rangle}{\partial \beta} \right) + \left\langle \left(\mathbf{a}^\dagger \mathbf{a} + \frac{1}{2} \right) \right\rangle^2$$

Now, when the zero-point energy is ignored, Eq. (13.53) remains true so that it is possible to write

$$\langle (\mathbf{a}^\dagger \mathbf{a})^2 \rangle = -\frac{1}{\hbar\omega} \left(\frac{\partial \ \langle \mathbf{a}^\dagger \mathbf{a} \ \rangle}{\partial \beta} \right) + \ \langle \mathbf{a}^\dagger \mathbf{a} \rangle^2$$

or, due to Eq. (13.35),

$$\langle \mathbf{n}^2 \rangle = -\frac{1}{\hbar\omega} \left(\frac{\partial \langle \mathbf{n} \rangle}{\partial \beta} \right) + \langle \mathbf{n} \rangle^2 \tag{13.54}$$

Hence, comparing Eq. (13.36), that is,

$$\langle \mathbf{n} \rangle = \left(\frac{1}{e^{\beta\hbar\omega} - 1} \right) \tag{13.55}$$

Eq. (13.54) reads

$$\langle \mathbf{n}^2 \rangle = -\frac{1}{\hbar\omega} \left(\frac{\partial}{\partial \beta} \left(\frac{1}{e^{\beta\hbar\omega} - 1} \right) \right) + \left(\frac{1}{e^{\beta\hbar\omega} - 1} \right)^2 \tag{13.56}$$

Next, evaluating the partial derivative of the first right-hand-side term leads to

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

so that Eq. (13.56) simplifies to

$$\langle\mathbf{n}^2\rangle = \left(\frac{e^{\beta\hbar\omega}+1}{(e^{\beta\hbar\omega}-1)^2}\right)$$

or

$$\langle\mathbf{n}^2\rangle = \frac{e^{\beta\hbar\omega}-1+2}{(e^{\beta\hbar\omega}-1)^2}$$

and thus

$$\langle\mathbf{n}^2\rangle = \frac{1}{e^{\beta\hbar\omega}-1} + \frac{2}{(e^{\beta\hbar\omega}-1)^2}$$

Hence, comparing Eq. (13.55), we have

$$\langle\mathbf{n}^2\rangle = \langle\mathbf{n}\rangle + 2\langle\mathbf{n}\rangle^2 \tag{13.57}$$

Now, by definition of the $\Delta\mathbf{n}$ thermal fluctuation

$$\Delta\mathbf{n} = \sqrt{\langle\mathbf{n}^2\rangle - \langle\mathbf{n}\rangle^2}$$

and with Eq. (13.57) this fluctuation becomes

$$\boxed{\Delta\mathbf{n} = \sqrt{\langle\mathbf{n}\rangle^2 + \langle\mathbf{n}\rangle}} \tag{13.58}$$

a result that is widely used in the area of the theory of lasers. Equation (13.58) may be also written

$$\Delta\mathbf{n} = \langle\mathbf{n}\rangle\sqrt{1+\frac{1}{\langle\mathbf{n}\rangle}}$$

Then, when

$$\langle\mathbf{n}\rangle >> 1$$

the argument of the square root may be expanded up to first order in $1/\langle\mathbf{n}\rangle$ according to

$$\sqrt{1+\frac{1}{\langle\mathbf{n}\rangle}} \backsimeq 1 + \frac{1}{2\langle\mathbf{n}\rangle}$$

so that in this limit

$$\Delta\mathbf{n} = \langle\mathbf{n}\rangle + \tfrac{1}{2}$$

Hence, in this limit, the relative fluctuations read

$$\frac{\Delta\mathbf{n}}{\langle\mathbf{n}\rangle} \backsimeq 1 + \frac{1}{2\langle\mathbf{n}\rangle} \backsimeq 1$$

13.2.6.3 Thermal average of Q, Q², and the potential We now consider the thermal equilibrium value of the position operator $\mathbf{Q}$ and of its square $\mathbf{Q}^2$, which are given, respectively, by the following thermal average over the Boltzmann density operator $\boldsymbol{\rho}_B$:

$$\langle \mathbf{Q}(T) \rangle = \mathbf{tr}\{\boldsymbol{\rho}_B \mathbf{Q}\} \qquad \text{and} \qquad \langle \mathbf{Q}(T)^2 \rangle = \mathbf{tr}\{\boldsymbol{\rho}_B \mathbf{Q}^2\} \tag{13.59}$$

Recall that within the raising and lowering operators picture of oscillators, $\mathbf{Q}$ is given by Eq. (5.6), that is,

$$\mathbf{Q} = \sqrt{\frac{\hbar}{2m\omega}}(\mathbf{a}^\dagger + \mathbf{a}) \tag{13.60}$$

whereas the Boltzmann density operator is given by Eqs. (13.23) and (13.24):

$$\boldsymbol{\rho}_B = (1 - e^{-\lambda})(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}}) \tag{13.61}$$

Hence, the thermal average defined by the first equation of (13.59) is, therefore,

$$\langle \mathbf{Q}(T) \rangle = (1 - e^{-\lambda})\sqrt{\frac{\hbar}{2m\omega}}\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(\mathbf{a}^\dagger + \mathbf{a})\}$$

Performing the trace over the eigenstates $|\{n\}\rangle$ of $\mathbf{a}^\dagger \mathbf{a}$ gives

$$\langle \mathbf{Q}(T) \rangle = (1 - e^{-\lambda})\sqrt{\frac{\hbar}{2m\omega}}\sum_n \langle \{n\}|(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(\mathbf{a}^\dagger + \mathbf{a})|\{n\}\rangle \tag{13.62}$$

Moreover, since $\mathbf{a}^\dagger \mathbf{a}$ is Hermitian

$$\mathbf{a}^\dagger \mathbf{a}|\{n\}\rangle = n|\{n\}\rangle$$

with

$$\langle \{m\}|\{n\}\rangle = \delta_{mn} \tag{13.63}$$

the two following Hermitian conjugate eigenvalue equations involved in Eq. (13.62) are verified:

$$(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})|\{n\}\rangle = (e^{-\lambda n})|\{n\}\rangle \qquad \text{and} \qquad \langle \{n\}|(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}}) = \langle \{n\}|(e^{-\lambda n}) \tag{13.64}$$

Hence, the right-hand side of (13.62) becomes

$$\langle \{n\}|(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(\mathbf{a}^\dagger + \mathbf{a})|\{n\}\rangle = (e^{-\lambda n})\langle \{n\}|(\mathbf{a}^\dagger + \mathbf{a})|\{n\}\rangle \tag{13.65}$$

Again, owing to Eqs. (5.53) and of its Hermitian conjugate, that is,

$$\mathbf{a}|\{n\}\rangle = \sqrt{n}|\{n-1\}\rangle \qquad \text{and thus} \qquad \langle \{n\}|\mathbf{a}^\dagger = \sqrt{n}\langle \{n-1\}|$$

and due to the orthogonality (13.63), Eq. (13.65) becomes

$$\langle \{n\}|(\mathbf{a}^\dagger + \mathbf{a})|\{n\}\rangle = \sqrt{n}\langle \{n-1\}|\{n\}\rangle + \sqrt{n}\langle \{n\}|\{n-1\}\rangle = 0$$

so that Eq. (13.65) transforms to

$$\langle \{n\}|(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(\mathbf{a}^\dagger + \mathbf{a})|\{n\}\rangle = 0 \tag{13.66}$$

Hence, the equilibrium thermal average value (13.62) is zero.

Next pass to the thermal average value of $\mathbf{Q}^2$, which, according to Eqs. (13.60) and (13.61), is

$$\langle \mathbf{Q}(T)^2 \rangle = (1 - e^{-\lambda}) \frac{\hbar}{2m\omega} \mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(\mathbf{a}^\dagger + \mathbf{a})^2\}$$

Expanding the square using $[\mathbf{a}, \mathbf{a}^\dagger] = 1$, gives

$$\langle \mathbf{Q}(T)^2 \rangle = (1 - e^{-\lambda}) \frac{\hbar}{2m\omega} (\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(2\mathbf{a}^\dagger \mathbf{a} + 1)\} + \mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})((\mathbf{a}^\dagger)^2 + (\mathbf{a})^2)\}) \tag{13.67}$$

Now, observe that, owing to Eq. (13.32) the first right-hand-side term of Eq. (13.67) is

$$(1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(2\mathbf{a}^\dagger \mathbf{a} + 1)\} = (2\langle \mathbf{n} \rangle + 1) \tag{13.68}$$

with

$$\langle \mathbf{n} \rangle = \frac{1}{e^\lambda - 1} \tag{13.69}$$

Now, perform trace over the basis of the eigenstates of $\mathbf{a}^\dagger \mathbf{a}$ appearing on the last right-hand-side term of Eq. (13.67)

$$\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})((\mathbf{a}^\dagger)^2 + (\mathbf{a})^2)\} = \sum_n \langle \{n\}|(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})((\mathbf{a}^\dagger)^2 + (\mathbf{a})^2)|\{n\}\rangle$$

which, due to the last equation of (13.64), this trace reads

$$\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})((\mathbf{a}^\dagger)^2 + (\mathbf{a})^2)\} = \sum_n (e^{-\lambda n})\langle \{n\}|((\mathbf{a}^\dagger)^2 + (\mathbf{a})^2)|\{n\}\rangle \tag{13.70}$$

Then, using Eqs. (5.71) and its Hermitian conjugate leads to the following Hermitian conjugate linear transformations:

$$(\mathbf{a})^2|\{n\}\rangle = \sqrt{n(n-1)}|\{n-2\}\rangle \qquad \text{and} \qquad \langle \{n\}|(\mathbf{a}^\dagger)^2 = \sqrt{n(n-1)}\langle \{n-2\}|$$

and by orthogonality of the eigenstates of $\mathbf{a}^\dagger \mathbf{a}$, Eq. (13.70) gives

$$\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})((\mathbf{a}^\dagger)^2 + (\mathbf{a})^2)\} = \sum_n 2((e^{-\lambda n})\sqrt{n(n-1)}\delta_{n,n-2})$$

and thus

$$\mathbf{tr}\{e^{-\lambda \mathbf{a}^\dagger \mathbf{a}}((\mathbf{a}^\dagger)^2 + (\mathbf{a})^2)\} = 0 \tag{13.71}$$

Hence, comparing Eqs. (13.68) and (13.71), Eq. (13.67) becomes simply

$$\boxed{\langle \mathbf{Q}(T)^2 \rangle = \frac{\hbar}{2m\omega}(2\langle \mathbf{n} \rangle + 1)} \tag{13.72}$$

or, using Eq. (13.69)

$$\langle \mathbf{Q}(T)^2 \rangle = \frac{\hbar}{2m\omega}\left(\frac{2}{e^\lambda - 1} + 1\right)$$

that is,

$$\langle \mathbf{Q}(T)^2 \rangle = \frac{\hbar}{2m\omega}\left(\frac{1 + e^\lambda}{e^\lambda - 1}\right)$$

Again, multiplying both numerator and denominator by the same quantity $\exp(-\lambda/2)$ to get

$$\langle \mathbf{Q}(T)^2 \rangle = \frac{\hbar}{2m\omega}\left(\frac{e^{\lambda/2}+e^{-\lambda/2}}{e^{\lambda/2}-e^{-\lambda/2}}\right) \tag{13.73}$$

with

$$\coth\left(\frac{\lambda}{2}\right) = \left(\frac{e^{\lambda/2}+e^{-\lambda/2}}{e^{\lambda/2}-e^{-\lambda/2}}\right) \tag{13.74}$$

$$\langle \mathbf{Q}(T)^2 \rangle = \frac{\hbar}{2m\omega}\coth\left(\frac{\lambda}{2}\right)$$

to obtain finally, by aid of Eq. (13.24), that is,

$$\lambda = \frac{\hbar\omega}{k_B T} \tag{13.75}$$

the following expression:

$$\langle \mathbf{Q}(T)^2 \rangle = \frac{\hbar}{2m\omega}\coth\left(\frac{\hbar\omega}{2k_B T}\right) \tag{13.76}$$

Hence, the thermal average $\langle \mathbf{V}(T) \rangle$ of the potential operator

$$\langle \mathbf{V}(T) \rangle = \tfrac{1}{2}m\omega^2 \langle \mathbf{Q}(T)^2 \rangle \tag{13.77}$$

becomes, comparing Eq. (13.76),

$$\langle \mathbf{V}(T) \rangle = \frac{\hbar\omega}{4}\coth\left(\frac{\hbar\omega}{2k_B T}\right) \tag{13.78}$$

Next, when the absolute temperature is such that $k_B T >> \hbar\omega$, so that, due to Eq. (13.75), $\lambda << 1$, the coth appearing in Eq. (13.73), yields after Taylor expansion up to first order

$$\left(\frac{e^{\lambda/2}+e^{-\lambda/2}}{e^{\lambda/2}-e^{-\lambda/2}}\right) \backsimeq \frac{(1+\lambda/2)+(1-\lambda/2)}{(1+\lambda/2)-(1-\lambda/2)} = \frac{2}{\lambda}$$

Then, the coth function reads with the help of Eq. (13.75):

$$\coth\left(\frac{\hbar\omega}{2k_B T}\right) \backsimeq \frac{k_B T}{2\hbar\omega} \quad \text{when} \quad k_B T > \hbar\omega$$

so that, for this high-temperature limit, Eqs. (13.76) and (13.77) simplify to

$$\langle \mathbf{Q}(T)^2 \rangle \backsimeq \frac{\hbar}{2m\omega}\left(\frac{2k_B T}{\hbar\omega}\right) = \frac{k_B T}{m\omega^2} \tag{13.79}$$

$$\langle \mathbf{V}(T) \rangle = \frac{k_B T}{2} \tag{13.80}$$

In the case of very low temperatures, corresponding to $\hbar\omega >> k_B T$, due to (13.75), when $\lambda >> 1$

$$\left(\frac{e^{\lambda/2}+e^{-\lambda/2}}{e^{\lambda/2}-e^{-\lambda/2}}\right) \backsimeq \left(\frac{e^{\lambda/2}}{e^{\lambda/2}}\right) \backsimeq 1$$

the coth function reduces to unity, that is,

$$\coth\left(\frac{\hbar\omega}{2k_BT}\right) \simeq 1 \quad \text{when} \quad \hbar\omega > k_BT$$

thus, in the very low temperature limit, Eqs. (13.76) and (13.77) reduce to

$$\langle \mathbf{Q}(0)^2 \rangle = \frac{\hbar}{2m\omega}$$

$$\langle \mathbf{V}(0) \rangle = \frac{\hbar\omega}{4} \tag{13.81}$$

In Eq. (13.81), one may recognize the mean value of the potential of the harmonic oscillator averaged over the ground state $|\{0\}\rangle$ of the harmonic oscillator Hamiltonian. Finally, the fluctuation of the position coordinate at any temperature T, which is defined by

$$\Delta\mathbf{Q}(T) = \sqrt{\langle \mathbf{Q}(T)^2 \rangle - \langle \mathbf{Q}(T) \rangle^2}$$

becomes, in view of Eqs. (13.62), (13.66), and (13.76),

$$\boxed{\Delta\mathbf{Q}(T) = \sqrt{\frac{\hbar}{2m\omega}}\sqrt{\coth\left(\frac{\hbar\omega}{2k_BT}\right)}} \tag{13.82}$$

13.2.6.4 Thermal average of P, P², and the kinetic operator In like manner as for $\mathbf{Q}(T)$ given by Eq. (13.62), one would obtain for the thermal average of the momentum

$$\langle \mathbf{P}(T) \rangle = 0 \tag{13.83}$$

and for the thermal average of the squared momentum, an expression similar to that (13.72) obtained for $\mathbf{Q}(T)^2$, that is, in the present situation

$$\langle \mathbf{P}(T)^2 \rangle = \frac{\hbar m\omega}{2}(2\langle \mathbf{n} \rangle + 1) \tag{13.84}$$

or, similarly to Eq. (13.76),

$$\langle \mathbf{P}(T)^2 \rangle = \frac{\hbar m\omega}{2}\coth\left(\frac{\hbar\omega}{2k_BT}\right) \tag{13.85}$$

Via this last expression, the thermal average value of the kinetic energy yields, respectively, for very high and very low temperatures is given by

$$\langle \mathbf{T}(T) \rangle = \frac{\hbar\omega}{4}\coth\left(\frac{\hbar\omega}{2k_BT}\right) \tag{13.86}$$

$$\langle \mathbf{T}(T) \rangle = \frac{k_BT}{2} \quad \text{when} \quad k_BT > \hbar\omega \tag{13.87}$$

$$\langle \mathbf{T}(0) \rangle = \frac{\hbar\omega}{4} \tag{13.88}$$

so that, comparing Eqs. (13.83) and (13.85), the fluctuation of $\mathbf{P}(T)$ is

$$\boxed{\Delta\mathbf{P}(T) = \sqrt{\frac{\hbar m\omega}{2}}\sqrt{\coth\left(\frac{\hbar\omega}{2k_B T}\right)}} \tag{13.89}$$

13.2.6.5 Verification of the virial theorem Now, for harmonic oscillators, the thermal average of the kinetic and potential energies obey the virial theorem (2.89), and since we deal with mean values averaged over linear combinations of harmonic oscillator Hamiltonian eigenstates (which are necessarily stationary states), it is not surprising to find that Eqs. (13.78) and (13.86) also obey this theorem (2.89) since

$$\langle\mathbf{T}(T)\rangle = \langle\mathbf{V}(T)\rangle = \frac{\hbar\omega}{4}\coth\left(\frac{\hbar\omega}{2k_B T}\right) \tag{13.90}$$

Furthermore, since the thermal averaged Hamiltonian is the sum of the thermal average kinetic and potential operators, it follows from Eq. (13.90) that the form of the virial theorem (2.89) holds also for any temperature

$$\langle\mathbf{H}(T)\rangle = 2\langle\mathbf{T}(T)\rangle = 2\langle\mathbf{V}(T)\rangle = \frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2k_B T}\right)$$

whereas, comparing Eqs. (13.80) and (13.87), its high-temperature limit is

$$\langle\mathbf{T}(T)\rangle = \langle\mathbf{V}(T)\rangle = \frac{k_B T}{2} \tag{13.91}$$

and, due to Eqs. (13.81) and (13.88), its low temperature yields

$$\langle\mathbf{T}(0)\rangle = \langle\mathbf{V}(0)\rangle = \frac{\hbar\omega}{2} \tag{13.92}$$

We remark that Eq. (13.92) is in agreement with the results (5.99) and (5.100) found for the average values of the kinetic and potential operators when the harmonic oscillator is in the ground state $|\{0\}\rangle$ of its Hamiltonian.

13.2.6.6 Equipartition theorem The fact that at high temperatures the thermal average values of the potential and of the kinetic operators are equal and given by Eq. (13.91) is an illustration of the *equipartition theorem* of classical statistical mechanics, according to which the thermal energy is quadratic with respect to the independent variables and is $k_B T/2$ for each degree of freedom. Now, we prove this theorem in a general way.

Suppose that the energy E of the system is quadratic with respect to N classical different continuous independent variables q_k, that is,

$$E = \sum_{k=1}^{N} E_k \quad \text{with} \quad E_k = \lambda_k {q_k}^2 \tag{13.93}$$

For each energy term E_k, its thermal average value may be obtained by Eq. (12.69):

$$\langle E_k(T)\rangle = -\left(\frac{\partial \ln Z_k}{\partial\beta}\right) \tag{13.94}$$

where Z_k is the partition function, which for continuous variable may be got from Eq. (12.67) by passing from the discrete sum to the corresponding integral according to

$$Z_k = \int_{-\infty}^{+\infty} e^{-\beta\lambda_k q_k{}^2} dq_k$$

which yields after integration

$$Z_k = \frac{1}{2}\sqrt{\frac{\pi}{\beta\lambda_k}}$$

so that

$$\ln Z_k = \ln\left(\frac{1}{2}\sqrt{\frac{\pi}{\lambda_k}}\right) - \frac{1}{2}\ln\beta$$

Hence, the thermal average (13.94) becomes

$$\langle E_k(T)\rangle = \frac{1}{2\beta} = \frac{k_B T}{2}$$

that is the *equipartition theorem* of classical statistical mechanics. As a consequence of this result and due to Eq. (13.93), the thermal average of the total energy $\langle E(T)\rangle$ is the number N of different independent variables times $k_B T/2$:

$$\langle E(T)\rangle = N\frac{k_B T}{2} = \frac{RT}{2}$$

where R is the ideal gas constant

13.2.6.7 Thermal Heisenberg uncertainty relation Now, we consider the thermal fluctuations of the position and momentum operators. Owing to Eqs. (13.82) and (13.89), the product of the thermal average of the uncertainty relation reads

$$\Delta\mathbf{P}(T)\ \Delta\mathbf{Q}(T) = \frac{\hbar}{2}\coth\left(\frac{\hbar\omega}{2k_B T}\right)$$

or, in view of the expression of the coth function,

$$\Delta\mathbf{P}(T)\ \Delta\mathbf{Q}(T) = \frac{\hbar}{2}\left(\frac{e^{\hbar\omega/2k_B T} + e^{-\hbar\omega/2k_B T}}{e^{\hbar\omega/2k_B T} - e^{-\hbar\omega/2k_B T}}\right) \tag{13.95}$$

When the absolute temperature approaches zero, the arguments of the decreasing exponential also narrow to zero. Thus, after simplification, one obtains the limit

$$\Delta\mathbf{P}(T)\ \Delta\mathbf{Q}(T) \to \frac{\hbar}{2} \quad \text{when} \quad T \to 0$$

As required by Eq. (5.96), this limit corresponds to the lowest Heisenberg uncertainty (5.97) obtained for the ground state of the harmonic oscillator.

Also, when the absolute temperature is very large, that is, when $k_B T > \hbar\omega$, Taylor expansions of the exponentials the arguments of which are very small may be limited to first order, that is,

$$e^{\pm\hbar\omega/2k_B T} = 1 \pm \hbar\omega/2k_B T$$

so that, for this high-temperature limit, Eq. (13.95) reduces to

$$\Delta\mathbf{P}(T)\ \Delta\mathbf{Q}(T) = \frac{\hbar}{2}\left(\frac{2}{\hbar\omega/2k_BT}\right)$$

or

$$\Delta\mathbf{P}(T)\ \Delta\mathbf{Q}(T) = 2\hbar\left(\frac{k_BT}{\hbar\omega}\right)$$

13.2.7 Coherent-state density operator at thermal equilibrium

13.2.7.1 Density operator from the Lagrange multipliers method We now determine the expression for the density operator of a coherent state at thermal equilibrium. Thus, it is convenient to work in the same way as when obtaining the canonical and microcanonical density operators (12.49) and (12.63) using the Lagrange multipliers method. Thus, consider a population of equivalent harmonic oscillators for which one knows the entropy and the average value of the Hamiltonian **H** of the position operator **Q** and of its conjugate momentum **P**. Then, the normalization condition of the density operator $\boldsymbol{\rho}_c$, the expression of the statistical entropy S in terms of $\boldsymbol{\rho}_c$, and the average values of **H** , **Q**, and **P** lead, respectively, to

$$\mathbf{tr}\{\boldsymbol{\rho}_c \ln \boldsymbol{\rho}_c\} = S \tag{13.96}$$

$$\mathbf{tr}\{\boldsymbol{\rho}_c\} = 1 \tag{13.97}$$

$$\mathbf{tr}\{\boldsymbol{\rho}_c\mathbf{H}\} = \langle\mathbf{H}\rangle \tag{13.98}$$

$$\mathbf{tr}\{\boldsymbol{\rho}_c\mathbf{Q}\} = \langle\mathbf{Q}\rangle \tag{13.99}$$

$$\mathbf{tr}\{\boldsymbol{\rho}_c\mathbf{P}\} = \langle\mathbf{P}\rangle \tag{13.100}$$

Just as for Eq. (12.47), the equation dealing with the maximization $dS = 0$ of the statistical entropy S is

$$\mathbf{tr}\{(1 + \ln \boldsymbol{\rho}_c)\delta\boldsymbol{\rho}_c\} = 0$$

Moreover, due to the constraints linked to Eqs. (13.96)–(13.100), leading to

$$\mathbf{tr}\{\delta\boldsymbol{\rho}_c\} = 0 \tag{13.101}$$

$$\mathbf{tr}\{\mathbf{H}\delta\boldsymbol{\rho}_c\} = 0 \tag{13.102}$$

$$\mathbf{tr}\{\mathbf{Q}\delta\boldsymbol{\rho}_c\} = 0 \tag{13.103}$$

$$\mathbf{tr}\{\mathbf{P}\delta\boldsymbol{\rho}_c\} = 0 \tag{13.104}$$

one has, according to the Lagrange multipliers method, to multiply each of them by Lagrange multipliers according to

$$\lambda_0\ \mathbf{tr}\{\delta\boldsymbol{\rho}_c\} = 0 \tag{13.105}$$

$$\beta\, \mathbf{tr}\{\mathbf{H}\delta\boldsymbol{\rho}_c\} = 0 \tag{13.106}$$

$$\lambda_1\, \mathbf{tr}\{\mathbf{Q}\delta\boldsymbol{\rho}_c\} = 0 \tag{13.107}$$

$$\lambda_2\, \mathbf{tr}\{\mathbf{P}\delta\boldsymbol{\rho}_c\} = 0 \tag{13.108}$$

where λ_0, β, λ_1, and λ_2 are, respectively, the Lagrange parameters associated to the constraints (13.101)–(13.104).

Next, collecting the constraints multiplied by the corresponding Lagrange multipliers, we have maximizing the statistical entropy

$$\mathbf{tr}\{(1 + \ln \boldsymbol{\rho}_c + \lambda_0 + \beta\mathbf{H} + \lambda_1\mathbf{Q} + \lambda_2\mathbf{P})\delta\boldsymbol{\rho}_c\} = 0$$

Hence, since this last equation must be satisfied irrespective of the basis on which the trace is performed, we have

$$1 + \ln\{\boldsymbol{\rho}_c\} + \lambda_0 + \beta\mathbf{H} + \lambda_1\mathbf{P} + \lambda_2\mathbf{Q} = 0$$

or, by integration,

$$\boldsymbol{\rho}_c = e^{-(1+\lambda_0)-\beta\mathbf{H}+\lambda_1\mathbf{Q}+\lambda_2\mathbf{P}}$$

or, since λ_0 is a scalar,

$$\boldsymbol{\rho}_c = e^{-(1+\lambda_0)}e^{-(\beta\mathbf{H}-\lambda_1\mathbf{Q}-\lambda_2\mathbf{P})} \tag{13.109}$$

where ω is the angular frequency of the oscillator and m its reduced mass. Again, express the position operator and its momentum conjugate and also the Hamiltonian in which the zero-point energy is ignored, in terms of the Boson operators according to

$$\mathbf{Q} = \sqrt{\frac{\hbar}{2m\omega}}(\mathbf{a}^\dagger + \mathbf{a}) \qquad \text{and} \qquad \mathbf{P} = i\sqrt{\frac{\hbar m\omega}{2}}(\mathbf{a}^\dagger - \mathbf{a})$$

$$\mathbf{H} = \hbar\omega\, \mathbf{a}^\dagger\mathbf{a}$$

so that the argument of the last exponential of the right-hand side of Eq. (13.109) is

$$\lambda_1\mathbf{PQ} + \lambda_2\mathbf{P} = i\lambda_2 m\omega\sqrt{\frac{\hbar}{2m\omega}}(\mathbf{a}^\dagger - \mathbf{a}) + \lambda_1\sqrt{\frac{\hbar}{2m\omega}}(\mathbf{a}^\dagger + \mathbf{a})$$

or

$$\lambda_1\mathbf{PQ} + \lambda_2\mathbf{P} = \sqrt{\frac{\hbar}{2m\omega}}\{\mathbf{a}^\dagger(\lambda_1 + i\lambda_2 m\omega) + \mathbf{a}(\lambda_1 - i\lambda_2 m\omega)\}$$

Now, let

$$\lambda = \hbar\omega\beta$$

$$\alpha = \frac{1}{\lambda}\sqrt{\frac{\hbar}{2m\omega}}(\lambda_1 + i\lambda_2 m\omega) \qquad \text{and} \qquad \alpha^* = \frac{1}{\lambda}\sqrt{\frac{\hbar}{2m\omega}}(\lambda_1 - i\lambda_2 m\omega)$$

so that

$$\beta\mathbf{H} + \lambda_1\mathbf{Q} + \lambda_2\mathbf{P} = -\lambda(\mathbf{a}^\dagger\mathbf{a} + \alpha^*\mathbf{a} + \alpha\mathbf{a}^\dagger)$$

13.2.7.2 Some properties In terms of these new scalar and operator variables, the density operator (13.109) takes the form

$$\boldsymbol{\rho}_c = e^{-(1+\lambda_0)}e^{-\lambda(\mathbf{a}^\dagger\mathbf{a}+\alpha\mathbf{a}^\dagger+\alpha^*\mathbf{a})}$$

Next, in order to normalize, as required, the density operator, assume that

$$e^{-(1+\lambda_0)} = (1-e^{-\lambda})e^{-\lambda|\alpha|^2} \tag{13.110}$$

Then, the density operator, which will appear later to be normalized, reads

$$\boldsymbol{\rho}_c = (1-e^{-\lambda})e^{-\lambda(\mathbf{a}^\dagger\mathbf{a}+\alpha\mathbf{a}^\dagger+\alpha^*\mathbf{a}+|\alpha|^2)}$$

or

$$\boxed{\boldsymbol{\rho}_c = (1-e^{-\lambda})e^{-\lambda(\mathbf{a}^\dagger+\alpha)(\mathbf{a}+\alpha^*)}} \tag{13.111}$$

Next, perform the following canonical transformation:

$$\mathbf{A}(\alpha)\boldsymbol{\rho}_c\mathbf{A}(\alpha)^{-1} = (1-e^{-\lambda})\mathbf{A}(\alpha)e^{-\lambda(\mathbf{a}^\dagger+\alpha)(\mathbf{a}+\alpha^*)}\mathbf{A}(\alpha)^{-1} \tag{13.112}$$

with

$$\mathbf{A}(\alpha) = (e^{\alpha^*\mathbf{a}^\dagger-\alpha\mathbf{a}})$$

Next, due to Eqs. (7.9) and (7.10), which read

$$\mathbf{A}(\alpha)\{\mathbf{f}(\mathbf{a},\mathbf{a}^\dagger)\}\mathbf{A}(\alpha)^{-1} = \{\mathbf{f}(\mathbf{a}-\alpha^*,\mathbf{a}^\dagger-\alpha)\}$$

Eq. (13.112) yields

$$\mathbf{A}(\alpha)\boldsymbol{\rho}_c\mathbf{A}(\alpha)^{-1} = (1-e^{-\lambda})(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})$$

a result that, according to Eq. (13.22), is the Boltzmann density operator, leading to

$$\mathbf{A}(\alpha)\boldsymbol{\rho}_c\mathbf{A}(\alpha)^{-1} = \boldsymbol{\rho}_B \tag{13.113}$$

Observe that, since the Boltzmann density operator is normalized, and since a canonical transformation does not modify the normalization, it appears that $\boldsymbol{\rho}_c$ has been, indeed, normalized by the assumption.

Now, the coherent-state density operator reduces at zero temperature to the pure coherent-state density operator built up from a coherent state. For this purpose, inverse Eq. (13.113), so that

$$\boldsymbol{\rho}_c = \mathbf{A}(\alpha)^{-1}\mathbf{A}(\alpha)\boldsymbol{\rho}_c\mathbf{A}(\alpha)^{-1}\mathbf{A}(\alpha) = \mathbf{A}(\alpha)^{-1}\boldsymbol{\rho}_B\mathbf{A}(\alpha)$$

or, due to Eq. (13.22),

$$\boldsymbol{\rho}_c = (1-e^{-\lambda})\mathbf{A}(\alpha)^{-1}(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\mathbf{A}(\alpha)$$

Now, insert between the Boltzmann density operator and the translation operator a closure relation over the eigenstates of $\mathbf{a}^\dagger\mathbf{a}$, that is,

$$\boldsymbol{\rho}_c = (1-e^{-\lambda})\mathbf{A}(\alpha)^{-1}(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\sum_n |\{n\}\rangle\langle\{n\}|\mathbf{A}(\alpha)$$

Then, with the eigenvalue equation of $\mathbf{a}^\dagger\mathbf{a}$, the coherent-state density operator reads

$$\boldsymbol{\rho}_c = (1-e^{-\lambda})\mathbf{A}(\alpha)^{-1}\sum_n(e^{-\lambda n})|\{n\}\rangle\langle\{n\}|\mathbf{A}(\alpha)$$

Next, if the temperature vanishes, λ which is given by Eq. (13.24), that is,

$$\lambda = \frac{\hbar\omega}{k_B T}$$

becomes infinite, so that

$$e^{-\lambda} \to 0$$

$$e^{-\lambda n} = e^{-n\hbar\omega/k_B T} \to 0 \quad \text{if} \quad n \neq 0$$

$$e^{-\lambda n} = e^{-n\hbar\omega/k_B T} = 1 \quad \text{if} \quad n = 0$$

Hence, the sum over the n eigenstates of $\mathbf{a}^\dagger \mathbf{a}$ reduces to the ground state, so that the coherent density operator reduces to

$$\{\boldsymbol{\rho}_c(T=0)\} = \mathbf{A}(\alpha)^{-1}|\{0\}\rangle\langle\{0\}|\mathbf{A}(\alpha)$$

or, comparing Eq. (6.92),

$$\{\boldsymbol{\rho}_c(T=0)\} = |\{\tilde{\alpha}\}\rangle\langle\{\tilde{\alpha}\}|$$

with

$$\mathbf{a}|\{\tilde{\alpha}\}\rangle = -\alpha|\{\tilde{\alpha}\}\rangle$$

Hence, when the absolute temperature vanishes, the density operator $\{\boldsymbol{\rho}_c(T=0)\}$ reduces to a coherent state $|\{\tilde{\alpha}\}\rangle$ of eigenvalue $-\alpha$, and so is the reason for its name.

13.2.8 Entropy of oscillators at thermal equilibrium

To get now an expression for the classical entropy of a population of oscillators at thermal equilibrium, which is the purpose of the present subsection, one has first to find an expression for the differential of the partition function in terms of the differential changes in the statistical parameter β and of the thermal average differential work $\langle dW \rangle$.

Hence, we first calculate $\langle dW \rangle$ and start from the differential expression of the 1D mechanical work along the x abscissa, that is,

$$dW = -F(x)\,dx \quad \text{with} \quad F(x) = -\left(\frac{\partial E(x)}{\partial x}\right)dx$$

and thus, when the energy $E(x)$ is quantized and defined by the energy levels $E_n(x)$,

$$dW_n = \left(\frac{\partial E_n(x)}{\partial x}\right)dx$$

the thermal average of the differential work is the average over the Boltzmann distribution of the different dW_n, that is,

$$\langle dW \rangle = \frac{1}{Z_\mu}\sum_n e^{-\beta E_n(x)}\left(\frac{\partial E_n(x)}{\partial x}\right)dx \quad \text{with} \quad Z_\mu = \sum_n e^{-\beta E_n(x)} \quad \text{and} \quad \beta = \frac{1}{k_B T}$$

where Z_μ is the partition function of a single oscillator. This expression may be also written

$$\langle dW \rangle = -\frac{1}{Z_\mu \beta} \sum_n \left(\frac{\partial e^{-\beta E_n(x)}}{\partial x} \right) dx$$

Moreover, since the sum and the partial derivative commute,

$$\langle dW \rangle = -\frac{1}{Z_\mu \beta} \frac{\partial}{\partial x} \sum_n e^{-\beta E_n(x)} dx = -\frac{1}{Z_\mu \beta} \left(\frac{\partial Z_\mu}{\partial x} \right) dx = -\frac{1}{\beta} \left(\frac{\partial \ln Z_\mu}{\partial x} \right) dx \tag{13.114}$$

Next, the total differential of $\ln Z_\mu(x, \beta)$ viewed as a function of the independent variables x and β reads

$$d\{\ln Z_\mu(x, \beta)\} = \left(\frac{\partial \ln Z_\mu}{\partial x} \right) dx + \left(\frac{\partial \ln Z_\mu}{\partial \beta} \right) d\beta \tag{13.115}$$

The thermal average Hamiltonian $\langle \mathbf{H} \rangle$, that is, the thermal energy, is given by Eq. (12.69):

$$\langle \mathbf{H} \rangle = -\left(\frac{\partial \ln Z_\mu}{\partial \beta} \right) \tag{13.116}$$

Hence, due to Eqs. (13.114) and (13.116), the total differential (13.115) yields

$$d\{\ln Z_\mu(x, \beta)\} = -\beta \langle dW \rangle - \langle \mathbf{H} \rangle d\beta$$

or

$$d\{\ln Z_\mu(x, \beta)\} = -\beta \langle dW \rangle - d\{\langle \mathbf{H} \rangle \beta\} + \beta d\langle \mathbf{H} \rangle$$

and thus

$$d\{\ln Z_\mu + (\langle \mathbf{H} \rangle \beta)\} = \beta\{d\langle \mathbf{H} \rangle - \langle dW \rangle\} \tag{13.117}$$

Then, recognizing in the difference between $d\langle \mathbf{H} \rangle$ and $\langle dW \rangle$ the differential heat exchange dQ, and using for β, Eq. (13.14), Eq. (13.117) reads

$$d\left\{\ln Z_\mu + \frac{\langle \mathbf{H} \rangle}{k_B T}\right\} = \frac{dQ}{k_B T}$$

Now, multiplying both terms of this last equation by the Boltzmann constant k_B and recognizing on the left-hand side the thermodynamical expression of the differential entropy dS, this expression becomes

$$k_B d\left\{\ln Z_\mu + \frac{\langle \mathbf{H} \rangle}{k_B T}\right\} = \frac{dQ}{T} = dS$$

Hence, the canonical entropy takes the form

$$\boxed{S = k_B \ln Z_\mu + \frac{\langle \mathbf{H} \rangle}{T}} \tag{13.118}$$

Equation (13.118) holds for one particle at thermal equilibrium, Z_μ and $\langle \mathbf{H} \rangle$ being, respectively, the partition function and the thermal average of this single particle. For N particles and because the partition function is the sum over exponentials, the partition function Z must be the Nth power of Z_μ. However, since the particles are indistinguishable, according to Chapter 2 because of the Heisenberg uncertainty relations, this power must be divided by $N!$ in order to avoid redundancies due to indistinguishable situations. Therefore, for N particles, Eq. (13.118) becomes

$$S = k_B \frac{\ln (Z_\mu)^{nN^\circ}}{(nN^\circ)!} + \frac{nN^\circ \langle \mathbf{H} \rangle}{T} \quad \text{with} \quad N = nN^\circ \tag{13.119}$$

where N° is the Avogadro number and n the number of moles. Again, after using, respectively, for Z_μ and $\langle E \rangle$, Eqs. (13.21) and (13.29), the entropy (13.119) yields

$$\boxed{S = n \left\{ \frac{R}{(nN^\circ)!} \ln \left\{ \frac{(e^{\hbar\omega/2k_BT})}{1 - \; e^{\hbar\omega/k_BT}} \right\} + N^\circ \frac{\hbar\omega}{T} \left(\frac{1}{e^{\hbar\omega k_BT} - 1} + \frac{1}{2} \right) \right\}} \tag{13.120}$$

where R is the ideal gas constant.

13.2.9 Oscillator Helmholtz potential

In thermodynamics, the Helmholtz thermodynamic potential is defined by

$$F = U - TS$$

where U is the internal energy. Then, for a population of oscillators, one may assimilate U to the oscillator thermal energy, and thus it is possible to write

$$U = \langle \mathbf{H} \rangle$$

so that, using for the entropy Eq. (13.118) the thermodynamic potential reads after simplification

$$F = -k_B T \ln Z_\mu \tag{13.121}$$

where it must be remembered that the partition function Z_μ is related to the Boltzmann density operator via Eq. (13.13), that is,

$$Z_\mu = \mathbf{tr}\{e^{-\beta \mathbf{H}}\} \quad \text{with} \quad \beta = \frac{1}{k_B T}$$

Hence, it appears from Eq. (13.121) that

$$\boxed{e^{-\beta F} = Z_\mu \; = \mathbf{tr}\{e^{-\beta \mathbf{H}}\}} \tag{13.122}$$

For a population of harmonic oscillators in thermal equilibrium, Eq. (13.122) reads with the help of Eq. (13.21)

$$e^{-\beta F} = \frac{e^{-\lambda/2}}{1 - e^{-\lambda}} \quad \text{with} \quad \lambda = \frac{\hbar\omega}{k_B T}$$

so that the thermodynamic potential yields

$$F = \frac{1}{\beta} \ln(1 - e^{-\lambda}) + \frac{\lambda}{2\beta}$$

or

$$F = k_B T \ln(1 - e^{-\hbar\omega/k_B T}) + \frac{\hbar\omega}{2} \tag{13.123}$$

13.2.10 Anharmonic oscillators dilatation with temperature

The dilatation of a solid with temperature is a well-known physical observation. This thermal dilatation is a result of anharmonicity we desire to treat here, where the dilation with temperature will be obtained in a numerical way for 1D oscillator. Hence, consider the thermal average value of the Q coordinate of an anharmonic oscillator performed over the Boltzmann density operator.

First, the Hamiltonian of an anharmonic oscillator is given by

$$\mathbf{H} = \hbar\omega\left(\mathbf{a}^{\dagger}\mathbf{a} + \tfrac{1}{2}\right) + \lambda\hbar\omega(\mathbf{a}^{\dagger} + \mathbf{a})^3$$

Its eigenvalue equation is

$$\mathbf{H}|\Psi_k\rangle = E_k|\Psi_k\rangle \tag{13.124}$$

with

$$\langle\Psi_k|\Psi_l\rangle = \delta_{kl}$$

For a given value of λ, this equation may be numerically solved working in the basis where $\mathbf{a}^{\dagger}\mathbf{a}$ is diagonal. In this basis, the expansion of the eigenkets of $\mathbf{H}$ is given by

$$|\Psi_k\rangle = \sum_n C_{kn}|\{n\}\rangle \quad \text{with} \quad \mathbf{a}^{\dagger}\mathbf{a}\;|\{n\}\rangle = n|\{n\}\rangle \tag{13.125}$$

The thermal average of the $\mathbf{Q}$ coordinate is

$$\langle\mathbf{Q}(T)\rangle = \mathbf{tr}\{\boldsymbol{\rho}_B\mathbf{Q}\}$$

where the Boltzmann density operator is given by Eq. (13.13)

$$\boldsymbol{\rho}_B = \frac{1}{Z}(e^{-\beta\mathbf{H}}) \quad \text{with} \quad \beta = \frac{1}{k_BT} \qquad \text{and} \qquad Z = \mathbf{tr}\{e^{-\beta\mathbf{H}}\}$$

and where $\mathbf{Q}$ is given in terms of the Boson operators by Eq. (5.6), that is,

$$\mathbf{Q} = \sqrt{\frac{\hbar}{2m\omega}}(\mathbf{a}^{\dagger} + \mathbf{a})$$

Writing explicitly the thermal average of $\mathbf{Q}$ over the basis where the Hamiltonian $\mathbf{H}$ is diagonal gives

$$\langle\mathbf{Q}(T)\rangle = \frac{1}{Z}\sqrt{\frac{\hbar}{2m\omega}}\sum_k\langle\Psi_k|(e^{-\beta\mathbf{H}})(\mathbf{a}^{\dagger} + \mathbf{a})|\Psi_k\rangle$$

Then, according to Eq. (13.124), the action on the bra of the exponential operator gives

$$\langle\mathbf{Q}(T)\rangle = \frac{1}{Z}\sqrt{\frac{\hbar}{2m\omega}}\sum_k \exp\left(-\frac{E_k}{k_BT}\right)\langle\Psi_k|(\mathbf{a}^{\dagger} + \mathbf{a})|\Psi_k\rangle$$

Next, introduce after $(\mathbf{a}^{\dagger} + \mathbf{a})$ the closure relation built on the eigenstates of $\mathbf{a}^{\dagger}\mathbf{a}$ to get

$$\langle\mathbf{Q}(T)\rangle = \frac{1}{Z}\sqrt{\frac{\hbar}{2m\omega}}\sum_k\sum_n \exp\left(-\frac{E_k}{k_BT}\right)\langle\Psi_k|(\mathbf{a}^{\dagger} + \mathbf{a})|\{n\}\rangle\langle\{n\}|\,\Psi_k\rangle$$

or

$$\langle \mathbf{Q}(T) \rangle = \frac{1}{Z}\sqrt{\frac{\hbar}{2m\omega}} \sum_k \sum_n \exp\left(-\frac{E_k}{k_B T}\right) C_{nk} \langle \Psi_k | (\mathbf{a}^\dagger + \mathbf{a}) | \{n\} \rangle$$

with

$$C_{n,k} = \langle \{n\} | \Psi_k \rangle \tag{13.126}$$

Again, using the result of the action of **a** and $\mathbf{a}^\dagger$ on an eigenket of $\mathbf{a}^\dagger\mathbf{a}$ leads according to Eqs. (5.53) and (5.63) to

$$\begin{aligned}\langle \mathbf{Q}(T) \rangle &= \frac{1}{Z}\sqrt{\frac{\hbar}{2m\omega}} \sum_k \sum_n \exp\left(-\frac{E_k}{k_B T}\right) \\ &\quad \times C_{nk} \left(\sqrt{n+1}\langle \Psi_k | \{n+1\} \rangle + \sqrt{n}\langle \Psi_k | \{n-1\} \rangle\right)\end{aligned}$$

or, using in turn Eq. (13.126), the orthogonality of the eigenkets of $\mathbf{a}^\dagger\mathbf{a}$ and the result of the action of **a** and $\mathbf{a}^\dagger$ on an eigenket of $\mathbf{a}^\dagger\mathbf{a}$ leads to

$$\langle \mathbf{Q}(T) \rangle = \frac{1}{Z}\sqrt{\frac{\hbar}{2m\omega}} \sum_k \sum_n \exp\left(-\frac{E_k}{k_B T}\right) C_{nk} \left\{C_{k,n+1}\sqrt{n+1} + C_{k,n-1}\sqrt{n}\right\} \tag{13.127}$$

Equation (13.127) allows one to compute the variation with temperature of the average value of the elongation of the anharmonic oscillator from the knowledge of the **H** eigenvalues E_k and of the expansion coefficients C_{kn} of the corresponding eigenvectors.

Figure 13.3 gives the temperature evolution of $\langle \mathbf{Q}(T) \rangle$ calculated in this way by the aid of Eq. (13.127) from the E_k and C_{kn} computed with the help of Eqs. (9.50) and (9.51).

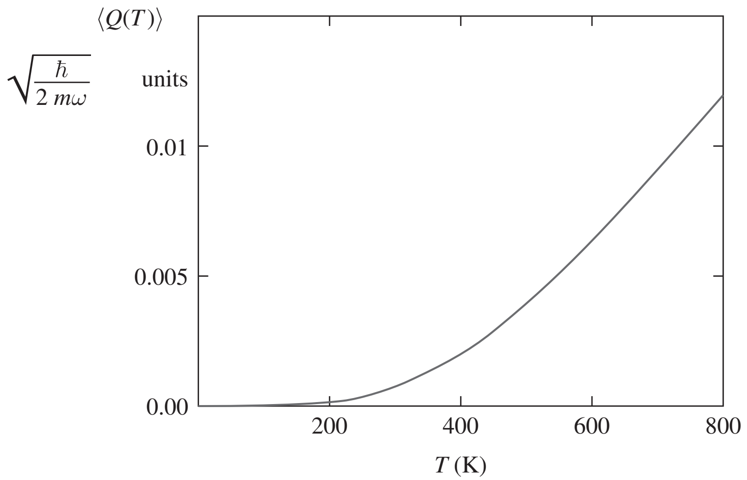

Figure 13.3 Temperature evolution of the elongation $\langle \mathbf{Q}(T) \rangle$ (in $Q^{\circ\circ} = \sqrt{\hbar/2m\omega}$ units) of an anharmonic oscillator. Anharmonic parameter $\beta = 0.017\hbar\omega$; number of basis states 75.

In three dimensions, the cube of Eq. (13.127) allows one to obtain the temperature dependence of the dilatation of a solid modelized by a 3D anharmonic oscillator. Observe that, according to Eqs. (13.62) and (13.66), which hold when the anharmonicity of the oscillator is missing, the average value of $\mathbf{Q}$ is zero for all quantum numbers so that the thermal average $\langle \mathbf{Q}(T) \rangle$ vanishes whatever the temperature.

13.3 HELMHOLTZ POTENTIAL FOR ANHARMONIC OSCILLATORS

Consider the Hamiltonian of an anharmonic oscillator of the form

$$\mathbf{H} = \mathbf{H}^\circ + \mathbf{V} \tag{13.128}$$

where $\mathbf{H}^\circ$ is the Hamiltonian of the harmonic oscillator and $\mathbf{V}$ the anharmonic Hamiltonian perturbation. Then, according to Eq. (13.12) the unnormalized Boltzmann density operator of the harmonic and anharmonic oscillators read, respectively,

$$\boldsymbol{\rho}^\circ \propto e^{-\beta \mathbf{H}^\circ} \quad \text{and} \quad \boldsymbol{\rho} \propto e^{-\beta \mathbf{H}} \tag{13.129}$$

Now, the partial differential of these density operators with respect to β read, respectively,

$$\left(\frac{\partial \boldsymbol{\rho}^\circ}{\partial \beta}\right) \propto -\mathbf{H}^\circ e^{-\beta \mathbf{H}^\circ} \qquad \text{and} \qquad \left(\frac{\partial \boldsymbol{\rho}}{\partial \beta}\right) \propto -\mathbf{H} e^{-\beta \mathbf{H}} \tag{13.130}$$

Next, in order to express $\boldsymbol{\rho}$ in terms of $\boldsymbol{\rho}^\circ$, first calculate

$$\left(\frac{\partial (e^{\beta \mathbf{H}^\circ} e^{-\beta \mathbf{H}})}{\partial \beta}\right) = \left(\frac{\partial e^{\beta \mathbf{H}^\circ}}{\partial \beta}\right) e^{-\beta \mathbf{H}} + e^{\beta \mathbf{H}^\circ} \left(\frac{\partial e^{-\beta \mathbf{H}}}{\partial \beta}\right) \tag{13.131}$$

which, due to (13.130), yields

$$\left(\frac{\partial (e^{\beta \mathbf{H}^\circ} e^{-\beta \mathbf{H}})}{\partial \beta}\right) = \mathbf{H}^\circ e^{\beta \mathbf{H}^\circ} e^{-\beta \mathbf{H}} - e^{\beta \mathbf{H}^\circ} \mathbf{H} e^{-\beta \mathbf{H}}$$

Or, since $\mathbf{H}^\circ$ commutes with the exponential constructed from it, and owing to Eq. (13.128),

$$\left(\frac{\partial (e^{\beta \mathbf{H}^\circ} e^{-\beta \mathbf{H}})}{\partial \beta}\right) = e^{\beta \mathbf{H}^\circ} (\mathbf{H}^\circ - \mathbf{H}) e^{-\beta \mathbf{H}} = -e^{\beta \mathbf{H}^\circ} \mathbf{V} e^{-\beta \mathbf{H}}$$

Due to Eq. (13.129), the latter equation leads to

$$d\{e^{\beta \mathbf{H}^\circ} \boldsymbol{\rho}(\beta)\} = -e^{\beta \mathbf{H}^\circ} \mathbf{V} e^{-\beta \mathbf{H}} \, d\beta$$

the integration of which from zero to β reads

$$\int_0^\beta d\{e^{\beta' \mathbf{H}^\circ} \boldsymbol{\rho}(\beta')\} = -\int_0^\beta e^{\beta' \mathbf{H}^\circ} \mathbf{V} e^{-\beta' \mathbf{H}} \, d\beta' \tag{13.132}$$

Now, observe that when $\beta = 0$, it appears from (13.129) that

$$e^{\beta \mathbf{H}^\circ} \boldsymbol{\rho}(\beta) = e^{\beta \mathbf{H}^\circ} e^{-\beta \mathbf{H}} = 1$$

so that the integration of (13.132) reads

$$e^{\beta \mathbf{H}^\circ} \boldsymbol{\rho}(\beta) - 1 = -\int_0^\beta e^{-(\beta-\beta')\mathbf{H}^\circ} \mathbf{V} e^{-\beta' \mathbf{H}}\, d\beta'$$

or, after premultiplying both members by $\exp\{-\beta \mathbf{H}^\circ\}$ and using the last expression of (13.129),

$$\boldsymbol{\rho}(\beta) = e^{-\beta \mathbf{H}^\circ} - \int_0^\beta e^{-(\beta-\beta')\mathbf{H}^\circ} \mathbf{V} \rho(\beta)\, d\beta'$$

The first-order solution of this last integral is

$$\boldsymbol{\rho}(\beta) = e^{-\beta \mathbf{H}^\circ} - \int_0^\beta e^{-(\beta-\beta')\mathbf{H}^\circ} \mathbf{V} e^{-\beta' \mathbf{H}^\circ}\, d\beta'$$

whereas the second-order solution is

$$\boldsymbol{\rho}(\beta) = e^{-\beta \mathbf{H}^\circ} - \int_0^\beta e^{-(\beta-\beta')\mathbf{H}^\circ} \mathbf{V} e^{-\beta' \mathbf{H}^\circ} d\beta' + \int_0^\beta \int_0^{\beta'} e^{-(\beta-\beta')\mathbf{H}^\circ} \mathbf{V} e^{-(\beta'-\beta'')\mathbf{H}^\circ} \times \mathbf{V} e^{-\beta'' \mathbf{H}^\circ} d\beta' d\beta'' \tag{13.133}$$

The solution (13.133) is dealing with a density operator that is unnormalized. But that is of no importance if one is interested in the Helmholtz energy F, which is related, via Eq. (13.122), to the Boltzmann density operator through

$$e^{-\beta F} = \mathbf{tr}\{e^{-\beta \mathbf{H}}\} = \mathbf{tr}\{\boldsymbol{\rho}(\beta)\} \tag{13.134}$$

an expression that is true whatever the normalization of the density operator. Hence, one gets

$$e^{-\beta F} = \mathbf{tr}\{e^{-\beta \mathbf{H}^\circ}\} - \int_0^\beta \mathbf{tr}\{e^{-(\beta-\beta')\mathbf{H}^\circ} \mathbf{V} e^{-\beta' \mathbf{H}^\circ}\} d\beta' + \int_0^\beta \int_0^{\beta'} \mathbf{tr}\{e^{-(\beta-\beta')\mathbf{H}^\circ} \mathbf{V} e^{-(\beta'-\beta'')\mathbf{H}^\circ} \mathbf{V} e^{-\beta'' \mathbf{H}^\circ}\}\, d\beta' d\beta'' \tag{13.135}$$

Now, due to the invariance of the trace with respect to a circular permutation within it, it appears that

$$\mathbf{tr}\{e^{-(\beta-\beta')\mathbf{H}^\circ} \mathbf{V} e^{-\beta' \mathbf{H}^\circ}\} = \mathbf{tr}\{e^{-\beta' \mathbf{H}^\circ} e^{-(\beta-\beta')\mathbf{H}^\circ} \mathbf{V}\} = \mathbf{tr}\{e^{-\beta \mathbf{H}^\circ} \mathbf{V}\} \tag{13.136}$$

$$\begin{aligned}\mathbf{tr}\{e^{-(\beta-\beta')\mathbf{H}^\circ}\mathbf{V}e^{-(\beta'-\beta'')\mathbf{H}^\circ}\mathbf{V}e^{-\beta''\mathbf{H}^\circ}\} &= \mathbf{tr}\{e^{-\beta''\mathbf{H}^\circ}e^{-(\beta-\beta')\mathbf{H}^\circ}\mathbf{V}e^{-(\beta'-\beta'')\mathbf{H}^\circ}\mathbf{V}\} \\ &= \mathbf{tr}\{e^{-\beta\mathbf{H}^\circ}e^{-(\beta''-\beta')\mathbf{H}^\circ}\mathbf{V}e^{-(\beta'-\beta'')\mathbf{H}^\circ}\mathbf{V}\}\end{aligned} \tag{13.137}$$

Moreover, perform the first trace over the eigenstates $|(n)\rangle$ of $\mathbf{H}^\circ$ to get

$$\mathbf{tr}\{e^{-\beta\mathbf{H}^\circ}\mathbf{V}\} = \sum_n \langle (n)|e^{-\beta\mathbf{H}^\circ}\mathbf{V}|(n)\rangle = \sum_n e^{-n\beta\hbar\omega}\langle (n)|\mathbf{V}|(n)\rangle \tag{13.138}$$

whereas working in the same way for the trace (13.137) and after inserting a closure relation over the basis $\{|(n)\rangle\}$ after the first operator $\mathbf{V}$ yields

$$\begin{aligned}&\mathbf{tr}\{e^{-\beta\mathbf{H}^\circ}e^{-(\beta''-\beta')\mathbf{H}^\circ}\mathbf{V}e^{-(\beta'-\beta'')\mathbf{H}^\circ}\mathbf{V}\} \\ &\quad = \sum_n\sum_m \langle (n)|e^{-\beta\mathbf{H}^\circ}e^{-(\beta''-\beta')\mathbf{H}^\circ}\mathbf{V}|(m)\rangle\langle (m)|e^{-(\beta'-\beta'')\mathbf{H}^\circ}\mathbf{V}|(n)\rangle\end{aligned}$$

or

$$\begin{aligned}&\mathbf{tr}\{e^{-\beta\mathbf{H}^\circ}e^{-(\beta''-\beta')\mathbf{H}^\circ}\mathbf{V}e^{-(\beta'-\beta'')\mathbf{H}^\circ}\mathbf{V}\} \\ &\quad = \sum_n\sum_m e^{-n\beta\hbar\omega}e^{-n(\beta''-\beta')\hbar\omega}\langle (n)|\mathbf{V}|(m)\rangle e^{-m(\beta'-\beta'')\hbar\omega}\langle (m)|\mathbf{V}|(n)\rangle\end{aligned} \tag{13.139}$$

Due to Eqs. (13.136) and (13.137) and to Eqs. (13.138) and (13.139), Eq. (13.135) giving the Helmholtz free energy becomes

$$\begin{aligned}e^{-\beta F} &= \mathbf{tr}\{e^{-\beta\mathbf{H}^\circ}\} - \sum_n e^{-n\beta\hbar\omega}\langle (n)|\mathbf{V}|(n)\rangle\int_0^\beta d\beta' \\ &\quad + \sum_n\sum_m e^{-n\beta\hbar\omega}|\langle (m)|\mathbf{V}|(n)\rangle^2|\int_0^\beta\int_0^{\beta'} e^{(n-m)\hbar\omega(\beta'-\beta'')}d\beta' d\beta''\end{aligned} \tag{13.140}$$

Now, observe the latter integral may be written

$$\int_0^\beta\int_0^{\beta'} e^{(n-m)\hbar\omega(\beta'-\beta'')}d\beta' d\beta'' = \frac{1}{2}\int_0^\beta e^{(n-m)\hbar\omega\eta}d\eta\int_0^\beta d\beta''$$

leading to

$$\int_0^\beta\int_0^{\beta'} e^{(n-m)\hbar\omega(\beta'-\beta'')}d\beta' d\beta'' = \frac{\beta}{2\hbar\omega}\frac{e^{(n-m)\beta\hbar\omega}-1}{n-m}$$

As a consequence, Eq. (13.140) takes the form

$$\boxed{e^{-\beta F} = e^{-\beta F^\circ} - \beta\sum_n e^{-n\beta\hbar\omega}\langle (n)|\mathbf{V}|(n)\rangle + \frac{\beta}{2\hbar\omega}\sum_n\sum_m |\langle (m)|\mathbf{V}|(n)\rangle^2|\frac{e^{-m\beta\hbar\omega}-e^{-n\beta\hbar\omega}}{(n-m)}} \tag{13.141}$$

with, in a similar way as in Eq. (13.134),

$$e^{-\beta F^\circ} = \mathbf{tr}\{e^{-\beta \mathbf{H}^\circ}\}$$

From Eq. (13.141), it may be shown[1] that

$$\boxed{F \leqslant F^\circ + \langle \mathbf{V} \rangle_0 \quad \text{with} \quad \langle \mathbf{V} \rangle_0 = \frac{\mathbf{tr}\{\mathbf{V} e^{-\beta \mathbf{H}^\circ}\}}{\mathbf{tr}\{e^{-\beta \mathbf{H}^\circ}\}}}$$

a result that allows one to find physical average values by minimization procedure. Besides, Eq. (13.141) may be applied to an anharmonic oscillator in which $\mathbf{V}$ is given by

$$\mathbf{V} = \left(\frac{\hbar}{2m\omega}\right)^{3/2} (\mathbf{a}^\dagger + \mathbf{a})^3$$

with the help of Eqs. (9.41)–(9.48) and using Eq. (13.21) allowing one to write

$$e^{-\beta F^\circ} = \mathbf{tr}\{e^{-\beta \mathbf{H}^\circ}\} = Z = \frac{e^{-\lambda/2}}{1 - e^{-\lambda}} \quad \text{with} \quad \lambda = \frac{\hbar\omega}{k_B T}$$

13.4 THERMAL AVERAGE OF BOSON OPERATOR FUNCTIONS

Now, we shall obtain the general expression for the average of any function of Boson operators over the Boltzmann equilibrium density operator. We shall obtain a general expression that reduces to the Bloch theorem when the function of Boson operators is either the position operator or its conjugate momentum. If the demonstration is somewhat tedious, it has the merit of avoiding the mathematical complications required to obtain its simplified form, which is the Bloch theorem.

13.4.1 Calculation of thermal average

In this section we derive the expression of the thermal average of any function of Boson operators over the canonical density operator of an harmonic oscillator, that is,

$$\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a}) \rangle = \mathbf{tr}\{\{\mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\}\rho_B(\mathbf{a}^\dagger, \mathbf{a})\}$$

which, in view of Eqs. (13.23) and (13.24), reads

$$\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a}) \rangle = (1 - e^{-\lambda})\mathbf{tr}\{\{\mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\}(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})\} \tag{13.142}$$

$$\lambda = \frac{\hbar\omega}{k_B T} \tag{13.143}$$

[1] R. P. Feynman. *Statistical Mechanics: A Set of Lectures*, 2nd ed. Perseus Books: New York, 1998.

13.4.1.1 From the basic equation (13.142) to a more tractable one Tracing on the right-hand side, over the eigenstates $|(n)\rangle$ of $\mathbf{a}^\dagger\mathbf{a}$, transforms Eq. (13.142) to

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \sum_n \langle (n)|\{\mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\}(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})|(n)\rangle \tag{13.144}$$

with

$$\mathbf{a}^\dagger \mathbf{a}|(n)\rangle = n|(n)\rangle \tag{13.145}$$

Now, observe that the only terms of $\mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})$, which may contribute to the diagonal matrix elements involved on the right-hand side of this last equation, are those having the same power of $\mathbf{a}^\dagger$ and $\mathbf{a}$.

Accordingly, in the trace above, we are free to change $\mathbf{a}$ into $k\mathbf{a}$ and $\mathbf{a}^\dagger$ into $\mathbf{a}^\dagger/k$ where k is some real scalar (that will be defined later). Hence, since the product $\mathbf{a}^\dagger\mathbf{a}$ involved in the density operator is not affected by this change, Eq. (13.144) yields

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \sum_n \langle (n)|\{\mathbf{F}(\mathbf{a}^\dagger/k, k\mathbf{a})\}(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})|(n)\rangle$$

Also we write this last equation in the following more complex form:

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \sum_n \sum_m \langle (n)|\{\mathbf{F}(\mathbf{a}^\dagger/k, k\mathbf{a})\}(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})|(m)\rangle \delta_{nm} \tag{13.146}$$

Moreover, due to Eqs. (5.69) and (5.70),

$$|(m)\rangle = \left(\frac{(\mathbf{a}^\dagger)^m}{\sqrt{m!}}\right)|(0)\rangle \qquad \text{and} \qquad \langle (n)| = \langle (0)|\left(\frac{(\mathbf{a})^n}{\sqrt{n!}}\right) \tag{13.147}$$

Equation (13.146) transforms to

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \sum_n \sum_m \langle (0)|\left(\frac{(\mathbf{a})^n}{\sqrt{n!}}\right)\{\mathbf{F}(\mathbf{a}^\dagger/k, k\mathbf{a})\}(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})\left(\frac{(\mathbf{a}^\dagger)^m}{\sqrt{m!}}\right)|(0)\rangle \delta_{nm} \tag{13.148}$$

Now, since the Kronecker symbol δ_{nm} appearing on the right-hand side of Eq (13.148) may be viewed as the scalar product of two eigenstates of any operator $\mathbf{b}^\dagger\mathbf{b}$, of Boson operators that commute with $\mathbf{a}^\dagger$ and $\mathbf{a}$, that is,

$$\delta_{nm} = \langle\{n\}|\{m\}\rangle \quad \text{with} \quad \mathbf{b}^\dagger\mathbf{b}|\{n\}\rangle = n|\{n\}\rangle \tag{13.149}$$

with

$$[\mathbf{a}, \mathbf{b}] = 0 \qquad [\mathbf{a}^\dagger, \mathbf{b}] = 0 \qquad [\mathbf{a}, \mathbf{b}^\dagger] = 0$$

Next, using for these Boson operators equations similar to those of (13.147),

$$|\{m\}\rangle = \left(\frac{(\mathbf{b}^\dagger)^m}{\sqrt{m!}}\right)|\{0\}\rangle \qquad \text{and} \qquad \langle\{n\}| = \langle\{0\}|\left(\frac{(\mathbf{b})^n}{\sqrt{n!}}\right)$$

the Kronecker symbol appearing in (13.149) becomes

$$\delta_{nm} = \langle\{0\}|\left(\frac{(\mathbf{b})^n}{\sqrt{n!}}\right)\left(\frac{(\mathbf{b}^\dagger)^m}{\sqrt{m!}}\right)|\{0\}\rangle \tag{13.150}$$

so that Eq. (13.148) reads

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \sum_n \sum_m \langle\{0\}|\langle(0)| \left(\frac{(\mathbf{b})^n}{\sqrt{n!}}\right)\left(\frac{(\mathbf{a})^n}{\sqrt{n!}}\right)$$
$$\times \{\mathbf{F}(\mathbf{a}^\dagger/k, k\mathbf{a})\}(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\left(\frac{(\mathbf{a}^\dagger)^m}{\sqrt{m!}}\right)\left(\frac{(\mathbf{b}^\dagger)^m}{\sqrt{m!}}\right)|(0)\rangle|\{0\}\rangle$$

Now, one may replace $\mathbf{b}$ by $\mu\mathbf{b}$ and $\mathbf{b}^\dagger$ by $\mathbf{b}^\dagger/\mu$, where μ is a real scalar, without modifying the right-hand-side average value, so that Eq. (13.150) becomes

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \sum_n \sum_m \langle\{0\}|\langle(0)| \left(\frac{(\mu\mathbf{b})^n}{\sqrt{n!}}\right)\left(\frac{(\mathbf{a})^n}{\sqrt{n!}}\right)$$
$$\times \{\mathbf{F}(\mathbf{a}^\dagger/k, k\mathbf{a})\}(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\left(\frac{(\mathbf{a}^\dagger)^m}{\sqrt{m!}}\right)\left(\frac{(\mathbf{b}^\dagger/\mu)^m}{\sqrt{m!}}\right)|(0)\rangle|\{0\}\rangle$$

or, rearranging and simplifying the notation for the ket or bra products,

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \sum_n \sum_m \langle\{0\}(0)| \left(\frac{(\mu\mathbf{ba})^n}{n!}\right)$$
$$\times \{\mathbf{F}(\mathbf{a}^\dagger/k, k\mathbf{a})\}(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\left(\frac{(\mathbf{a}^\dagger\mathbf{b}^\dagger/\mu)^m}{m!}\right)|(0)\{0\}\rangle$$

Then, pass to exponentials

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \langle\{0\}(0)|(e^{\mu\mathbf{ba}})\{\mathbf{F}(\mathbf{a}^\dagger/k, k\mathbf{a})\}(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\mathbf{a}^\dagger\mathbf{b}^\dagger/\mu})|(0)\{0\}\rangle$$

Furthermore, introduce after the function of Boson operators the unity operator defined by

$$1 = (e^{-\mu\mathbf{ba}})(e^{\mu\mathbf{ba}})$$

leading to

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \langle\{0\}(0)|(e^{\mu\mathbf{ba}})\{\mathbf{F}(\mathbf{a}^\dagger/k, k\mathbf{a})\}(e^{-\mu\mathbf{ba}})(e^{\mu\mathbf{ba}})(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\mathbf{a}^\dagger\mathbf{b}^\dagger/\mu})|(0)\{0\}\rangle \tag{13.151}$$

Now, according to Eq. (7.5), it appears that

$$(e^{\mu\mathbf{ba}})\{\mathbf{F}(\mathbf{a}^\dagger/k, k\mathbf{a})\}(e^{-\mu\mathbf{ba}}) = \{\mathbf{F}((\mathbf{a}^\dagger + \mu\mathbf{b})/k, k\mathbf{a})\} \tag{13.152}$$

and, comparing Eq. (7.106), that is,

$$(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{y\mathbf{a}^\dagger})|(0)\rangle = (e^{y\mathbf{a}^\dagger(e^{-\lambda})})|(0)\rangle$$

with

$$y = \frac{\mathbf{b}^\dagger}{\mu}$$

it appears that, since $\mathbf{b}^\dagger$ is dimensionless and does not act on the ket $|(0)\rangle$ because acting on $|\{0\}\rangle$ one finds

$$(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(e^{\mathbf{a}^\dagger \mathbf{b}^\dagger/\mu})|(0)\rangle = \{e^{\mathbf{a}^\dagger \mathbf{b}^\dagger e^{-\lambda}/\mu}\}|(0)\rangle \tag{13.153}$$

Hence, in view of Eqs. (13.152) and (13.153), the average value (13.151) simplifies to

$$\frac{\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle}{(1-e^{-\lambda})} = \langle \{0\}(0)|\{\mathbf{F}((\mathbf{a}^\dagger + \mu\mathbf{b})/k, k\mathbf{a})\}(e^{\mu\mathbf{ba}})\{e^{\xi\mathbf{a}^\dagger\mathbf{b}^\dagger}\}|(0)\{0\}\rangle \tag{13.154}$$

with

$$\xi = e^{-\lambda}/\mu \tag{13.155}$$

13.4.1.2 Action of the product of exponential operators involved in Eq. (13.154) on $|(0)\{0\}\rangle$ It is now required to find the action of the product of the two exponential operators involved on the right-hand side of Eq. (13.154) on the ground state $|(0)\{0\}\rangle$ of $\mathbf{a}^\dagger\mathbf{a}\,\mathbf{b}^\dagger\mathbf{b}$. Hence, one has to find a function of ladder operators $\mathbf{G}(\mu, \mathbf{a}^\dagger, \mathbf{b}^\dagger, \mathbf{a}, \mathbf{b})$ satisfying

$$(e^{\mathbf{G}(\mu,\mathbf{a}^\dagger,\mathbf{b}^\dagger,\mathbf{a},\mathbf{b})})|(0)\{0\}\rangle = (e^{\mu\mathbf{ba}})\{e^{\xi\mathbf{a}^\dagger\mathbf{b}^\dagger}\}|(0)\{0\}\rangle \tag{13.156}$$

For this purpose, differentiate both members of Eq. (13.156) with respect to μ, yielding

$$\exp(\mathbf{G})\left(\frac{\partial \mathbf{G}}{\partial \mu}\right)|(0)\{0\}\rangle = \mathbf{ba}(e^{\mu\mathbf{ba}})\{e^{\xi\mathbf{a}^\dagger\mathbf{b}^\dagger}\}|(0)\{0\}\rangle$$

or

$$\exp(\mathbf{G})\left(\frac{\partial \mathbf{G}}{\partial \mu}\right)|(0)\{0\}\rangle = \mathbf{ba}\;\exp\{\mathbf{G}\}|(0)\{0\}\rangle$$

Then, premultiplying both terms by $\exp(-\mathbf{G})$ we have

$$\left(\frac{\partial \mathbf{G}}{\partial \mu}\right)|(0)\{0\}\rangle = \exp\{-\mathbf{G}\}\mathbf{ba}\;\exp\{\mathbf{G}\}|(0)\{0\}\rangle$$

Again, insert between $\mathbf{b}$ and $\mathbf{a}$ the unity operator built up from $\exp\{-\mathbf{G}\}$, that is,

$$\left(\frac{\partial \mathbf{G}}{\partial \mu}\right)|(0)\{0\}\rangle = \exp\{-\mathbf{G}\}\,\mathbf{b}\{\mathbf{G}\}\exp\{-\mathbf{G}\}\mathbf{a}\;\exp\{\mathbf{G}\}|(0)\{0\}\rangle \tag{13.157}$$

and apply Eq. (7.60), that is,

$$\mathbf{af}(\mathbf{a}, \mathbf{a}^\dagger) - \mathbf{f}(\mathbf{a}, \mathbf{a}^\dagger)\mathbf{a} = \left(\frac{\partial \mathbf{f}(\mathbf{a}, \mathbf{a}^\dagger)}{\partial \mathbf{a}^\dagger}\right)$$

to the function

$$\mathbf{f}(\mathbf{a}, \mathbf{a}^\dagger) = \exp\{\mathbf{G}\}$$

Hence

$$\mathbf{a}\exp\{\mathbf{G}\} - \exp\{\mathbf{G}\}\mathbf{a} = \left(\frac{\partial \exp\{\mathbf{G}\}}{\partial \mathbf{a}^\dagger}\right)$$

or

$$\mathbf{a}\exp(\mathbf{G}) = \exp(\mathbf{G})\mathbf{a} + \exp\{\mathbf{G}\}\left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right)$$

Then, premultiplying both terms by $\exp(-\mathbf{G})$ we have after simplification

$$\exp\{-\mathbf{G}\}\mathbf{a}\exp\{\mathbf{G}\} = \mathbf{a} + \left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right) \tag{13.158}$$

In a similar way one would obtain

$$\exp\{-\mathbf{G}\}\mathbf{b}\exp\{\mathbf{G}\} = \mathbf{b} + \left(\frac{\partial \mathbf{G}}{\partial \mathbf{b}^\dagger}\right) \tag{13.159}$$

As a consequence of Eqs. (13.158) and (13.159), Eq. (13.157) becomes

$$\left(\frac{\partial \mathbf{G}}{\partial \mu}\right)|(0)\{0\}\rangle = \left(\mathbf{b} + \left(\frac{\partial \mathbf{G}}{\partial \mathbf{b}^\dagger}\right)\right)\left(\mathbf{a} + \left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right)\right)|(0)\{0\}\rangle$$

Then, performing the product involved on the right-hand side gives

$$\left(\frac{\partial \mathbf{G}}{\partial \mu}\right)|(0)\{0\}\rangle = \left(\mathbf{ba} + \left(\frac{\partial \mathbf{G}}{\partial \mathbf{b}^\dagger}\right)\left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right) + \mathbf{b}\left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right) + \left(\frac{\partial \mathbf{G}}{\partial \mathbf{b}^\dagger}\right)\mathbf{a}\right)|(0)\{0\}\rangle \tag{13.160}$$

Now, observe that since

$$\mathbf{b}|\{0\}\rangle = \mathbf{a}|(0)\rangle = 0 \tag{13.161}$$

we have

$$\mathbf{ba}|(0)\{0\}\rangle = \mathbf{b}|\{0\}\rangle\mathbf{a}|(0)\rangle = 0$$

so that Eq. (13.160) yields

$$\left(\frac{\partial \mathbf{G}}{\partial \mu}\right)|(0)\{0\}\rangle = \left(\left(\frac{\partial \mathbf{G}}{\partial \mathbf{b}^\dagger}\right)\left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right) + \mathbf{b}\left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right)\right)|(0)\{0\}\rangle \tag{13.162}$$

Again, using in turn Eq. (7.60),

$$\mathbf{bf}(\mathbf{b},\mathbf{b}^\dagger) - \mathbf{f}(\mathbf{b},\mathbf{b}^\dagger)\mathbf{b} = \left(\frac{\partial \mathbf{f}(\mathbf{b},\mathbf{b}^\dagger)}{\partial \mathbf{b}^\dagger}\right) \quad \text{with} \quad \mathbf{f}(\mathbf{b},\mathbf{b}^\dagger) = \left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right)$$

so that

$$\mathbf{b}\left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right) = \left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right)\mathbf{b} + \left(\frac{\partial^2 \mathbf{G}}{\partial \mathbf{b}^\dagger \partial \mathbf{a}^\dagger}\right)$$

and since, due to Eq. (13.161),

$$\left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right)\mathbf{b}|\{0\}\rangle = 0$$

Eq. (13.162) reads

$$\left(\frac{\partial \mathbf{G}}{\partial \mu}\right)|(0)\{0\}\rangle = \left(\left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right)\left(\frac{\partial \mathbf{G}}{\partial \mathbf{b}^\dagger}\right) + \left(\frac{\partial^2 \mathbf{G}}{\partial \mathbf{b}^\dagger\,\partial \mathbf{a}^\dagger}\right)\right)|(0)\{0\}\rangle \tag{13.163}$$

or

$$\left(\frac{\partial \mathbf{G}(\mathbf{a}^\dagger, \mathbf{b}^\dagger, \mu)}{\partial \mu}\right)|(0)\{0\}\rangle = \left(\frac{\partial \mathbf{G}}{\partial \mathbf{a}^\dagger}\right)\left(\frac{\partial \mathbf{G}}{\partial \mathbf{b}^\dagger}\right)\left(\frac{\partial^2 \mathbf{G}(\mathbf{a}^\dagger, \mathbf{b}^\dagger, \mu)}{\partial \mathbf{b}^\dagger\,\partial \mathbf{a}^\dagger}\right)|(0)\{0\}\rangle \quad (13.164)$$

Next, in order to solve this partial differential equation involving only $\mathbf{a}^\dagger$, $\mathbf{b}^\dagger$, and μ, one may seek a solution at an expression of the following form:

$$\mathbf{G}(\mathbf{a}^\dagger, \mathbf{b}^\dagger, \mu) = A(\mu) + B(\mu)\mathbf{a}^\dagger\mathbf{b}^\dagger \quad (13.165)$$

where $\mathbf{a}$ and $\mathbf{b}$ disappear, whereas $A(\mu)$ and $B(\mu)$ are unknown scalar coefficients. Now, in order to get the expression of the function (13.165) for the special situation where $\mu = 0$, use the fact that in this special situation, Eq. (13.156) reduces to

$$(e^{\mathbf{G}(0,\mathbf{a}^\dagger,\mathbf{b}^\dagger)})|(0)\{0\}\rangle = \{e^{\xi\mathbf{a}^\dagger\mathbf{b}^\dagger}\}|(0)\{0\}\rangle \quad (13.166)$$

Thereby, since the arguments of the exponentials appearing on the right- and on the left-hand-side operators of this last equation must be the same, we have

$$\mathbf{G}(0, \mathbf{a}^\dagger, \mathbf{b}^\dagger) = \xi\mathbf{a}^\dagger\mathbf{b}^\dagger$$

Thus, the comparison of this last expression with Eq. (13.165) in which $\mu = 0$ leads, respectively, to

$$A(0) = 0 \qquad \text{and} \qquad B(0) = \xi \quad (13.167)$$

Furthermore, due to Eq. (13.165), it appears that the partial derivative of $\mathbf{G}$ with respect to μ reads

$$\left(\frac{\partial \mathbf{G}(\mu, \mathbf{a}^\dagger, \mathbf{b}^\dagger)}{\partial \mu}\right) = \left(\frac{\partial A(\mu)}{\partial \mu}\right) + \left(\frac{\partial B(\mu)}{\partial \mu}\right)\mathbf{a}^\dagger\mathbf{b}^\dagger \quad (13.168)$$

while, the crossed second-order partial derivative of $\mathbf{G}$ with respect to $\mathbf{a}^\dagger$ and $\mathbf{b}^\dagger$ yields

$$\left(\frac{\partial^2 \mathbf{G}(\mu, \mathbf{a}^\dagger, \mathbf{b}^\dagger)}{\partial \mathbf{b}^\dagger\partial \mathbf{a}^\dagger}\right) = B(\mu) + \{B(\mu)\}^2\mathbf{a}^\dagger\mathbf{b}^\dagger \quad (13.169)$$

At last, due to Eq. (13.165)

$$\left(\frac{\partial \mathbf{G}(\mu, \mathbf{a}^\dagger, \mathbf{b}^\dagger)}{\partial \mathbf{a}^\dagger}\right) = B(\mu)\mathbf{b}^\dagger \qquad \text{and} \qquad \left(\frac{\partial \mathbf{G}(\mu, \mathbf{a}^\dagger, \mathbf{b}^\dagger)}{\partial \mathbf{b}^\dagger}\right) = B(\mu)\mathbf{a}^\dagger$$

so that, since $\mathbf{a}^\dagger$ and $\mathbf{b}^\dagger$ commute,

$$\left(\frac{\partial \mathbf{G}(\mu, \mathbf{a}^\dagger, \mathbf{b}^\dagger)}{\partial \mathbf{a}^\dagger}\right)\left(\frac{\partial \mathbf{G}(\mu, \mathbf{a}^\dagger, \mathbf{b}^\dagger)}{\partial \mathbf{b}^\dagger}\right) = \{B(\mu)\}^2\mathbf{a}^\dagger\mathbf{b}^\dagger \quad (13.170)$$

Hence, due to Eqs. (13.168)–(13.170), Eq. (13.164) takes the form

$$\left(\left(\frac{\partial A(\mu)}{\partial \mu}\right) + \left(\frac{\partial B(\mu)}{\partial \mu}\right)\mathbf{a}^\dagger\mathbf{b}^\dagger\right)|(0)\{0\}\rangle = (\{B(\mu)\} + \{B(\mu)\}^2\mathbf{a}^\dagger\mathbf{b}^\dagger)|(0)\{0\}\rangle$$

so that one obtains by identification

$$\left(\frac{\partial B(\mu)}{\partial \mu}\right) = \{B(\mu)\}^2 \quad (13.171)$$

$$\left(\frac{\partial A(\mu)}{\partial \mu}\right) = B(\mu) \tag{13.172}$$

By integration Eq. (13.171) yields

$$\mu = -\left(\frac{1}{B(\mu)} - \frac{1}{B(0)}\right)$$

or, in view of the boundary condition appearing in (13.167),

$$\mu = -\left(\frac{1}{B(\mu)} - \frac{1}{\xi}\right)$$

and thus, after rearranging,

$$B(\mu) = \frac{\xi}{1 - \xi\mu} \tag{13.173}$$

Next, insert this result into Eq. (13.172) to get

$$\left(\frac{\partial A(\mu)}{\partial \mu}\right) = \frac{\xi}{1 - \xi\mu}$$

which by integration yields

$$A(\mu) - A(0) = \xi \int_0^{\mu} \frac{d\mu'}{1 - \xi\mu'}$$

and thus, due to the first boundary condition of Eq. (13.167), and after calculation of the integral

$$A(\mu) = -\ln(1 - \xi\mu) \tag{13.174}$$

Hence, comparing Eq. (13.173), the function (13.165) becomes

$$\mathbf{G}(\mathbf{a}^\dagger, \mathbf{b}^\dagger, \mu) = -\ln(1 - \xi\mu) + \frac{\xi}{1 - \xi\mu}\mathbf{a}^\dagger\mathbf{b}^\dagger$$

so that Eq. (13.156) is

$$(e^{\mathbf{G}(\mu,\mathbf{a}^\dagger,\mathbf{b}^\dagger)})|(0)\{0\}\rangle = \exp\left\{\frac{\xi\mathbf{a}^\dagger\mathbf{b}^\dagger}{1 - \xi\mu} - \ln(1 - \xi\mu)\right\}|(0)\{0\}\rangle$$

or

$$(e^{\mathbf{G}(\mu,\mathbf{a}^\dagger,\mathbf{b}^\dagger)})|(0)\{0\}\rangle = \exp\left\{\frac{\xi\mathbf{a}^\dagger\mathbf{b}^\dagger}{1 - \xi\mu}\right\}\left(\frac{1}{(1 - \xi\mu)}\right)|(0)\{0\}\rangle$$

Now, observe that, due to Eq. (13.165), the left-hand side of this last equation is the same as that of (13.156), so that of the identification of the corresponding right-hand sides gives

$$(e^{\mu\mathbf{ba}})\{e^{\xi\mathbf{a}^\dagger\mathbf{b}^\dagger}\}|(0)\{0\}\rangle = \left(\frac{1}{(1 - \xi\mu)}\right)\exp\left\{\frac{\xi\mathbf{a}^\dagger\mathbf{b}^\dagger}{1 - \xi\mu}\right\}|(0)\{0\}\rangle \tag{13.175}$$

At last, coming back from ξ to λ by the aid of Eq. (13.155) leading to

$$\left(\frac{1}{(1 - \xi\mu)}\right) = \frac{1}{1 - e^{-\lambda}}$$

Eq. (13.175) transforms to

$$(e^{\mu \mathbf{ba}})\{e^{\mathbf{a}^\dagger \mathbf{b}^\dagger e^{-\lambda}/\mu}\}|(0)\{0\}\rangle = \frac{1}{(1-e^{-\lambda})}\{e^{\xi \mathbf{a}^\dagger \mathbf{b}^\dagger/(1-\xi\mu)}\}|(0)\{0\}\rangle \tag{13.176}$$

13.4.1.3 Final step for the thermal average value As a consequence of Eq. (13.176), the thermal average value (13.154) becomes

$$\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle = \langle\{0\}(0)|\{\mathbf{F}((\mathbf{a}^\dagger + \mu\mathbf{b})/k, k\mathbf{a})\}(e^{\mathbf{a}^\dagger \mathbf{b}^\dagger(\xi/(1-\xi\mu))})|(0)\{0\}\rangle \tag{13.177}$$

Again, observe that, owing to Eq. (13.155), it yields

$$\frac{\xi}{1-\xi\mu} = \frac{1}{\mu}\left(\frac{e^{-\lambda}}{1-e^{-\lambda}}\right) \tag{13.178}$$

Hence, due to Eqs. (13.14) and (13.36) we have

$$\langle \mathbf{n}\rangle = \frac{1}{e^{\lambda}-1} = \frac{e^{-\lambda}}{1-e^{-\lambda}} \quad \text{with} \quad \lambda = \frac{\hbar\omega}{k_B T} \tag{13.179}$$

where $\langle \mathbf{n}\rangle$ is the thermal average of the occupation number, that is, of $\mathbf{a}^\dagger\mathbf{a}$ or of $\mathbf{b}^\dagger\mathbf{b}$, that is,

$$\langle \mathbf{n}\rangle = (1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})\mathbf{a}^\dagger\mathbf{a}\} = (1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda \mathbf{b}^\dagger \mathbf{b}})\mathbf{b}^\dagger\mathbf{b}\}$$

Equation (13.178) reads

$$\frac{\xi}{1-\xi\mu} = \frac{\langle \mathbf{n}\rangle}{\mu} \tag{13.180}$$

so that the thermal average (13.177) yields

$$\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle = \langle\{0\}(0)\{|\mathbf{F}((\mathbf{a}^\dagger + \mu\mathbf{b})/k, k\mathbf{a})\}(e^{\langle \mathbf{n}\rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu})|(0)\{0\}\rangle \tag{13.181}$$

Now, observe that

$$\langle\{0\}(0)| = \langle\{0\}(0)|(e^{-\langle \mathbf{n}\rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) \tag{13.182}$$

that is because, after its expansion, the right-hand side reads

$$\langle\{0\}(0)|(e^{-\langle \mathbf{n}\rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) = \sum_m \langle\{0\}(0)|\left(\frac{\langle \mathbf{n}\rangle}{\mu}\right)^m \frac{(\mathbf{a}^\dagger)^m(\mathbf{b}^\dagger)^m(-1)^m}{m!}$$

or, after action of each operator within its own subspace,

$$\langle\{0\}(0)|(e^{-\langle \mathbf{n}\rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) = \sum_m (-1)^m \left(\frac{\langle \mathbf{n}\rangle}{\mu}\right)^m \frac{1}{m!}\langle\{0\}|(\mathbf{b}^\dagger)^m\langle(0)|(\mathbf{a})^m$$

then, using Eq. (5.73) leading to

$$\langle\{0\}|(\mathbf{b}^\dagger)^m = \langle(0)|(\mathbf{a}^\dagger)^m = \delta_{m,0}$$

it appears, Q.E.D.

$$\langle\{0\}(0)|(e^{-\langle \mathbf{n}\rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) = \langle\{0\}(0)|1$$

Therefore, Eq. (13.181) becomes

$$\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a}) \rangle = \langle \{0\}(0)|(e^{-\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu})\{\mathbf{F}((\mathbf{a}^\dagger + \mu \mathbf{b})/k, k\mathbf{a})\}(e^{\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu})|(0)\{0\}\rangle \tag{13.183}$$

Moreover, keeping in mind theorem (1.77) applying to some function $\mathbf{F}(\mathbf{B})$ of operator $\mathbf{B}$, that is,

$$e^{\xi \mathbf{A}}\, \mathbf{F}(\mathbf{B}) e^{-\xi \mathbf{A}} = \mathbf{F}(e^{\xi \mathbf{A}} \mathbf{B} e^{-\xi \mathbf{A}})$$

where ξ is a c-number and $\mathbf{A}$ is an operator that does not commute with $\mathbf{B}$, apply it to the canonical transformation appearing on the right-hand side of Eq. (13.183) by taking

$$\mathbf{A} = \mathbf{a}^\dagger \mathbf{b}^\dagger \qquad \xi = \frac{\langle \mathbf{n} \rangle}{\mu}$$

and

$$\mathbf{B} = \frac{\mathbf{a}^\dagger + \mu \mathbf{b}}{k} \qquad \text{or} \qquad \mathbf{B} = k\mathbf{a}$$

Then, this canonical transformation reads

$$\begin{aligned}
&(e^{-\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu})\{\mathbf{F}((\mathbf{a}^\dagger + \mu \mathbf{b})/k, k\mathbf{a})\}(e^{\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) \\
&= \mathbf{F}\left((e^{-\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) \left(\frac{\mathbf{a}^\dagger + \mu \mathbf{b}}{k} \right) (e^{\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}), k(e^{-\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) \mathbf{a} (e^{\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) \right)
\end{aligned} \tag{13.184}$$

Besides, since $\mathbf{a}^\dagger$ commutes with $\mathbf{b}^\dagger$, it is clear that

$$(e^{-\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu})\, \mathbf{a}^\dagger (e^{\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) = \mathbf{a}^\dagger$$

Moreover, applying theorem (7.7), that is,

$$e^{-\xi \mathbf{a}^\dagger} \mathbf{F}(\mathbf{a}, \mathbf{a}^\dagger) e^{\xi \mathbf{a}^\dagger} = \mathbf{F}(\mathbf{a} + \xi, \mathbf{a}^\dagger)$$

with taking

$$\xi = \frac{\langle \mathbf{n} \rangle}{\mu} \mathbf{a}^\dagger \qquad \text{or} \qquad \xi = \frac{\langle \mathbf{n} \rangle}{\mu} \mathbf{b}^\dagger$$

and keeping in mind the following commutators

$$[\mathbf{a}, \mathbf{b}^\dagger] = [\mathbf{a}^\dagger, \mathbf{b}^\dagger] = [\mathbf{a}^\dagger, \mathbf{b}] = [\mathbf{a}, \mathbf{b}] = 0$$

one finds, respectively,

$$(e^{-\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) \mathbf{b} (e^{\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) = \mathbf{b} + \frac{\langle \mathbf{n} \rangle}{\mu} \mathbf{a}^\dagger \tag{13.185}$$

$$(e^{-\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) \mathbf{a} (e^{\langle \mathbf{n} \rangle \mathbf{a}^\dagger \mathbf{b}^\dagger/\mu}) = \mathbf{a} + \frac{\langle \mathbf{n} \rangle}{\mu} \mathbf{b}^\dagger \tag{13.186}$$

As a consequence of Eqs. (13.185) and (13.186), the canonical transformation (13.184) becomes

$$(e^{\langle\mathbf{n}\rangle\mathbf{ab}/\mu})\{\mathbf{F}((\mathbf{a}^\dagger + \mu\mathbf{b})/k, k\mathbf{a})\}(e^{\langle\mathbf{n}\rangle\mathbf{a}^\dagger\mathbf{b}^\dagger/\mu})$$
$$= \left\{\mathbf{F}\left(\left(\frac{(1+\langle\mathbf{n}\rangle)}{k}\mathbf{a}^\dagger + \frac{\mu}{k}\mathbf{b}\right), \left(k\mathbf{a}+k\frac{\langle\mathbf{n}\rangle}{\mu}\mathbf{b}^\dagger\right)\right)\right\} \tag{13.187}$$

It is now necessary to find the expressions for the unknown scalars μ and k involved in this equation. For this purpose, we may write Eq. (13.187) in terms of two Boson operators $\mathbf{c}$ and $\mathbf{c}^\dagger$, which are linear combinations of $\mathbf{a}$ and $\mathbf{a}^\dagger$ and $\mathbf{b}$ and $\mathbf{b}^\dagger$ according to

$$(e^{\langle\mathbf{n}\rangle\mathbf{ab}/\mu})\{\mathbf{F}((\mathbf{a}^\dagger + \mu\mathbf{b})/k, k\mathbf{a})\}(e^{\langle\mathbf{n}\rangle\mathbf{a}^\dagger\mathbf{b}^\dagger/\mu}) = \{\mathbf{F}(\mathbf{c}^\dagger, \mathbf{c})\} \tag{13.188}$$

with

$$\mathbf{c} = C_1\mathbf{a}+C_2\mathbf{b}^\dagger \qquad \text{and} \qquad \mathbf{c}^\dagger = C_1^*\mathbf{a}^\dagger + C_2^*\mathbf{b} \tag{13.189}$$

so that after identification with the right-hand side of Eq. (13.187), one obtains, respectively, for the coefficients C_1 and C_2 of Eq. (13.189)

$$C_1 = k \qquad \text{and} \qquad C_2 = k\frac{\langle\mathbf{n}\rangle}{\mu} \tag{13.190}$$

$$C_1^* = \frac{(1+\langle\mathbf{n}\rangle)}{k} \qquad \text{and} \qquad C_2^* = \frac{\mu}{k} \tag{13.191}$$

Then, since the scalars k, μ, and $\langle\mathbf{n}\rangle$ appearing in Eqs. (13.190) and (13.191) are real, we have

$$C_1 = C_1^* \qquad \text{and} \qquad C_2 = C_2^*$$

so that Eqs. (13.190) and (13.191) read

$$k = \frac{(1+\langle\mathbf{n}\rangle)}{k} \qquad \text{and} \qquad k\frac{\langle\mathbf{n}\rangle}{\mu} = \frac{\mu}{k}$$

leading to

$$k = \sqrt{1+\langle\mathbf{n}\rangle} \qquad \text{and} \qquad \mu = k\sqrt{\langle\mathbf{n}\rangle}$$

Furthermore, introducing these expressions for k and μ into Eq. (13.187), we have

$$(e^{\langle\mathbf{n}\rangle\mathbf{ab}/\mu})\{\mathbf{F}((\mathbf{a}^\dagger + \mu\mathbf{b})/k, k\mathbf{a})\}(e^{\langle\mathbf{n}\rangle\mathbf{a}^\dagger\mathbf{b}^\dagger/\mu})$$
$$= \mathbf{F}\left(\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{a}^\dagger + \sqrt{\langle\mathbf{n}\rangle}\mathbf{b}, \sqrt{1+\langle\mathbf{n}\rangle}\mathbf{a} + \sqrt{\langle\mathbf{n}\rangle}\mathbf{b}^\dagger\right)$$

Hence, using this result allows one to transform the thermal average (13.183) into

$$\langle\mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle = \langle\{0\}(0)|\{\mathbf{F}(\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{a}^\dagger + \sqrt{\langle\mathbf{n}\rangle}\mathbf{b}, \sqrt{1+\langle\mathbf{n}\rangle}\mathbf{a} + \sqrt{\langle\mathbf{n}\rangle}\mathbf{b}^\dagger)\}|(0)\{0\}\rangle$$

which due to the definition of $\langle \mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\rangle$ given by Eq. (13.142) reads

$$(1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\{\mathbf{F}(\mathbf{a}^\dagger, \mathbf{a})\}\}$$
$$= \langle\{0\}(0)|\{\mathbf{F}(\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{a}^\dagger + \sqrt{\langle\mathbf{n}\rangle}\mathbf{b}, \sqrt{1+\langle\mathbf{n}\rangle}\mathbf{a} + \sqrt{\langle\mathbf{n}\rangle}\mathbf{b}^\dagger)\}|(0)\{0\}\rangle \tag{13.192}$$

13.4.2 Thermal average of translation operators and Bloch theorem

Now, suppose that the operator function to be averaged and given by Eq. (13.192) is a translation operator, that is,

$$\langle\mathbf{A}(T)\rangle = (1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\{\mathbf{A}(\mathbf{a}^\dagger, \mathbf{a})\}\} \tag{13.193}$$

with

$$\mathbf{A}(\mathbf{a}^\dagger, \mathbf{a}) = \{e^{\alpha\mathbf{a}^\dagger - \alpha^*\mathbf{a}}\}$$

and thus

$$\langle\mathbf{A}(T)\rangle = (1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\{e^{\alpha\mathbf{a}^\dagger - \alpha^*\mathbf{a}}\}\} \tag{13.194}$$

Then, using Glauber's theorem (1.79), in order to factorize the right-hand-side exponential operators

$$\{e^{\alpha\mathbf{a}^\dagger - \alpha^*\mathbf{a}}\} = (e^{\alpha\mathbf{a}^\dagger})(e^{-\alpha^*\mathbf{a}})e^{-[\alpha\mathbf{a}^\dagger, -\alpha^*\mathbf{a}]/2} \tag{13.195}$$

with

$$e^{-[\alpha\mathbf{a}^\dagger, -\alpha^*\mathbf{a}]/2} = e^{|\alpha|^2[\mathbf{a}^\dagger, \mathbf{a}]/2} = (e^{-|\alpha|^2/2}) \tag{13.196}$$

using Eqs. (13.195) and (13.196), the thermal average (13.194) becomes

$$\langle\mathbf{A}(T)\rangle = (1 - e^{-\lambda})e^{-|\alpha|^2/2}\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\alpha\mathbf{a}^\dagger})(e^{-\alpha^*\mathbf{a}})\} \tag{13.197}$$

Now, apply theorem (13.192) to Eq. (13.197) in order to find the expression for its thermal average. Then, ignoring momentously the phase factor $e^{-|\alpha|^2/2}$, we have

$$(1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\alpha\mathbf{a}^\dagger})(e^{-\alpha^*\mathbf{a}})\}$$
$$= \langle(0)|\langle\{0\}|(e^{\alpha(\sqrt{\langle\mathbf{n}\rangle}\mathbf{a}^\dagger + \sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b})})(e^{-\alpha^*(\sqrt{\langle\mathbf{n}\rangle}\mathbf{a} + \sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}^\dagger)})|\{0\}_2\rangle|\{0\}_1\rangle$$

Then, factorizing both exponentials, each involving commuting operators, gives

$$(1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\alpha\mathbf{a}^\dagger})(e^{-\alpha^*\mathbf{a}})\}$$
$$= \langle(0)|\langle\{0\}|(e^{\alpha\sqrt{\langle\mathbf{n}\rangle}\mathbf{a}^\dagger})(e^{\alpha\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}})(e^{-\alpha^*\sqrt{\langle\mathbf{n}\rangle}\mathbf{a}})(e^{-\alpha^*\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}^\dagger})|\{0\}\rangle|(0)\rangle$$

Again, working within the two different subspaces leads to

$$(1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\alpha(t)\mathbf{a}^\dagger})(e^{-\alpha^*(t)\mathbf{a}})\}$$
$$= \langle(0)|\{(e^{\alpha\sqrt{\langle\mathbf{n}\rangle}\mathbf{a}^\dagger})(e^{-\alpha^*\sqrt{\langle\mathbf{n}\rangle}\mathbf{a}})\}|(0)\rangle\langle\{0\}|\{(e^{\alpha\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}})(e^{-\alpha^*\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}^\dagger})\}|\{0\}\rangle \tag{13.198}$$

Next, expand the two exponentials of the last right-hand-side matrix element of this last equation to get

$$\langle\{0\}|\{(e^{\alpha\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}})(e^{-\alpha^*\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}^\dagger})\}|\{0\}\rangle$$
$$= \sum_k\sum_l(-1)^l\frac{\alpha^k\alpha^{*l}}{k!l!}(\sqrt{1+\langle\mathbf{n}\rangle})^{k+l}\langle(0)|\{(\mathbf{b})^k(\mathbf{b}^\dagger)^l\}|\{0\}\rangle \quad (13.199)$$

Then, comparing Eqs. (5.67) and (5.68), that is,

$$\langle\{0\}|(\mathbf{b})^k = \langle\{k\}|\sqrt{k!} \qquad \text{and} \qquad (\mathbf{b}^\dagger)^l\,|\{0\}\rangle = \sqrt{l!}|\{l\}\rangle$$

it appears that

$$\langle\{0\}|(\mathbf{b})^k(\mathbf{b}^\dagger)^l|(0)\rangle = \sqrt{k!}\sqrt{l!}\langle\{k\}|\{l\}\rangle = l!$$

so that the double sum of the matrix elements involved on the right-hand side of Eq. (13.199) reduces after simplifications to

$$\langle\{0\}|\{(e^{\alpha\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}})(e^{-\alpha^*\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}^\dagger})\}|\{0\}\rangle = \sum_l(-1)^l\frac{|\alpha|^{2l}}{l!}(\langle\mathbf{n}\rangle+1)^l$$

Therefore, coming back to the exponentials, this last equation becomes

$$\langle\{0\}|\{(e^{\alpha\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}})(e^{-\alpha^*\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{b}^\dagger})\}|\{0\}\rangle = \exp\{-|\alpha|^2(\langle\mathbf{n}\rangle+1)\} \quad (13.200)$$

Now, expand the exponential of the first matrix element of the right-hand side of Eq. (13.198), that is,

$$\langle(0)|\{(e^{\alpha\sqrt{\langle\mathbf{n}\rangle}\mathbf{a}^\dagger})(e^{-\alpha^*\sqrt{\langle\mathbf{n}\rangle}\mathbf{a}})\}|(0)\rangle$$
$$= \sum_k\sum_l(-1)^l\frac{\alpha^k\alpha^{*l}}{k!l!}(\sqrt{\langle\mathbf{n}\rangle})^{k+l}\langle(0)|\{(\mathbf{a}^\dagger)^k(\mathbf{a})^l\}|(0)\rangle \quad (13.201)$$

Then, owing to Eq. (5.55), we have

$$\langle(0)|(\mathbf{a}^\dagger)^k = 0 \quad \text{except if } k=0$$

$$(\mathbf{a})^l|(0)\rangle = 0 \quad \text{except if } l=0$$

This follows that Eq. (13.201) reduces to

$$\langle(0)|\{(e^{\alpha\sqrt{\langle\mathbf{n}\rangle}\mathbf{a}^\dagger})(e^{-\alpha^*\sqrt{\langle\mathbf{n}\rangle}\mathbf{a}})\}|(0)\rangle = 1 \quad (13.202)$$

As a consequence of Eqs. (13.200) and (13.202), the thermal average (13.198) becomes

$$(1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\alpha\mathbf{a}^\dagger})(e^{-\alpha^*\mathbf{a}})\} = \exp\{-|\alpha|^2(\langle\mathbf{n}\rangle+1)\} \quad (13.203)$$

with $\langle\mathbf{n}\rangle$ given by Eq. (13.179). Again, using Glauber's theorem yields

$$(1-e^{-\lambda})e^{-|\alpha|^2/2}\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\alpha\mathbf{a}^\dagger-\alpha^*\mathbf{a}})\}e^{|\alpha|^2} = \exp\{-|\alpha|^2(\langle\mathbf{n}\rangle+1)\}$$

so that after simplification

$$\boxed{\langle\mathbf{A}(T)\rangle = (1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\alpha\mathbf{a}^\dagger-\alpha^*\mathbf{a}})\} = \exp\left\{-|\alpha|^2\left(\langle\mathbf{n}\rangle+\tfrac{1}{2}\right)\right\}} \quad (13.204)$$

13.4.2.1 Bloch theorem Of course, one would obtain in a similar way as for Eq. (13.203)

$$(1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(e^{\alpha \mathbf{a}^\dagger + \alpha^* \mathbf{a}})\} = \exp\left\{|\alpha|^2 \left(\langle \mathbf{n} \rangle + \tfrac{1}{2}\right)\right\} \tag{13.205}$$

Next, if we denote and keep in mind Eqs. (5.6) allowing one to pass from the Boson operators to the position operator $\mathbf{Q}$ according to

$$\mathbf{Q} = \alpha(\mathbf{a}^\dagger + \mathbf{a}) \quad \text{with} \quad \alpha = \sqrt{\frac{\hbar}{2m\omega}}$$

it appears that if $\alpha(t)$ is real, the left-hand side of Eq. (13.205) reads

$$(1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(e^{\alpha(\mathbf{a}^\dagger + \mathbf{a})})\} = \mathbf{tr}\{\boldsymbol{\rho}_B e^{\mathbf{Q}}\} = \langle e^{\mathbf{Q}} \rangle \tag{13.206}$$

so that Eq. (13.205) yields

$$\langle e^{\mathbf{Q}} \rangle = \exp\left\{\frac{\hbar}{2m\omega}(\langle \mathbf{n} \rangle + \tfrac{1}{2})\right\} \tag{13.207}$$

Now, observe that the thermal average of $\mathbf{Q}(T)^2$ defined by

$$\langle \mathbf{Q}(T)^2 \rangle = \mathbf{tr}\{\boldsymbol{\rho}_B \mathbf{Q}(T)^2\}$$

that is,

$$\langle \mathbf{Q}(T)^2 \rangle = \frac{\hbar}{2m\omega}(1 - e^{-\lambda})\mathbf{tr}\{(e^{-\lambda \mathbf{a}^\dagger \mathbf{a}})(\mathbf{a}^\dagger + \mathbf{a})^2\}$$

is given by Eq. (13.72), that is,

$$\boxed{\langle \mathbf{Q}(T)^2 \rangle = \frac{\hbar}{2m\omega}(2\langle \mathbf{n} \rangle + 1)} \tag{13.208}$$

As a consequence of Eqs. (13.207) and (13.208),

$$\boxed{\langle e^{\mathbf{Q}} \rangle = e^{\langle \mathbf{Q}^2 \rangle /2}}$$

This last result is the *Bloch theorem*. In a similar way, one would obtain for the momentum

$$\boxed{\langle e^{\mathbf{P}} \rangle = e^{\langle \mathbf{P}^2 \rangle /2}}$$

13.5 CONCLUSION

Using the canonical operator, it was possible in this chapter to find many thermal properties of quantum harmonic oscillators such as the fundamental Planck law, the thermal average of kinetic and potential energies, the heat capacities, the energy fluctuations, and the part of the *Sackur and Tetrode law* dealing with entropy. Finally, we gave some complex demonstrations of the thermal average energy of ladder operator functions, one consequence of which is the Bloch theorem. The most important results dealing with thermal average of simple operators characterizing harmonic oscillators are reported as follows:

Thermal average over Boltzmann density operators
Boltzmann density operators:
$\boldsymbol{\rho}_B = \frac{1}{Z}(e^{-\beta \mathbf{H}}) \quad \text{with} \quad \beta = \frac{1}{k_B T}$
Partition function:
$Z = \left(\frac{e^{-\beta\hbar\omega/2}}{1 - \ e^{-\beta\hbar\omega}} \right)$
Average Hamiltonian:
$\langle \mathbf{H} \rangle = \left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \right)$
Heat capacity:
$C_v = N k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}$
Energy fluctuation:
$\Delta E_{\text{Tot}} = \sqrt{N} \hbar\omega \frac{e^{\hbar\omega/2k_B T}}{(e^{\hbar\omega/k_B T} - 1)}$
Average of $\mathbf{Q}^2$:
$\langle \mathbf{Q}(T)^2 \rangle = \frac{\hbar}{2m\omega} \coth\left(\frac{\hbar\omega}{2k_B T} \right)$
Entropy:
$S = n \left\{ \frac{R}{(nN^\circ)!} \ln\left\{ \frac{(e^{\hbar\omega/2k_B T})}{1 - \ e^{\hbar\omega/k_B T}} \right\} + N^\circ \frac{\hbar\omega}{T} \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} + \frac{1}{2} \right) \right\}$

whereas we give hereafter some important theorems dealing with the thermal average of exponential operators involving the ladder operators:

Theorems dealing with thermal averages
Thermal average of operators over Boltzmann density operator:
$(1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\{\mathbf{F}(\mathbf{a}^\dagger,\mathbf{a})\}\}$ $= \langle\{0\}(0)\|\{\mathbf{F}(\sqrt{1+\langle\mathbf{n}\rangle}\mathbf{a}^\dagger + \sqrt{\langle\mathbf{n}\rangle}\mathbf{b}, \sqrt{1+\langle\mathbf{n}\rangle}\mathbf{a} + \sqrt{\langle\mathbf{n}\rangle}\mathbf{b}^\dagger)\}\|(0)\{0\}\rangle$
Thermal average of the translation operator:
$(1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})(e^{\alpha\mathbf{a}^\dagger-\alpha^*\mathbf{a}})\} = \exp\{-\|\alpha\|^2(\langle\mathbf{n}\rangle + \frac{1}{2})\}$
Bloch's theorem:
$(1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})e^{\mathbf{Q}}\} = \exp\{(1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\mathbf{Q}^2/2\}\}$ $(1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})e^{\mathbf{P}}\} = \exp\{(1-e^{-\lambda})\mathbf{tr}\{(e^{-\lambda\mathbf{a}^\dagger\mathbf{a}})\mathbf{P}^2/2\}\}$

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