## Energy fluctuations in the canonical ensemble: correspondence with the microcanonical ensemble

In the canonical ensemble, a system can have energy anywhere between zero and infinity. On the other hand, the energy of a system in the microcanonical ensemble is restricted to a very narrow range. How, then, can we assert that the thermodynamic properties of a system derived through the formalism of the canonical ensemble would be the same as the ones derived through the formalism of the microcanonical ensemble? Of course, we do expect that the two formalisms yield identical results, for otherwise our whole scheme would be marred by inner inconsistency. And, indeed, in the case of an ideal classical gas the results obtained by following one approach were precisely the same as the ones obtained by following the other approach. What is the underlying reason for this equivalence?

The answer to this question is obtained by examining the *actual* extent of the range over which the energies of the systems (in the canonical ensemble) have a significant probability to spread; that will tell us the extent to which the canonical ensemble *really* differs from the microcanonical one. To do this, we write down the expression for the mean energy,

$$U \equiv \langle E \rangle = \frac{\sum_r E_r g_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}}$$

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_r E_r^2 g_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}} + \frac{\left[\sum_r E_r g_r e^{-\beta E_r}\right]^2}{\left[\sum_r g_r e^{-\beta E_r}\right]^2}$$

$$= -\left[\langle E^2 \rangle - \langle E \rangle^2\right] = -\langle (\Delta E)^2 \rangle$$

$$\langle (\Delta E)^2 \rangle \equiv \langle E^2 \rangle - \langle E \rangle^2 = -\left(\frac{\partial U}{\partial \beta}\right)$$

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

$$\frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} = \frac{\sqrt{(kT^2 C_V)}}{U} \sim \frac{\sqrt{N}}{N} \sim O(N^{-1/2})$$

$$if \quad N \to \infty \quad \Rightarrow O(N^{-1/2}) \to 0$$

$$P(E)dE \propto e^{-\beta E} g(E) dE$$

$$\frac{\partial}{\partial E}\left\{e^{-\beta E} g(E)\right\}\Big|_{E=E^*} = 0$$

$$-\beta e^{-\beta E^*} g(E^*) + e^{-\beta E^*} \frac{\partial g(E)}{\partial E}\Big|_{E=E^*} = 0$$

$$\frac{1}{kT} = \frac{1}{g(E^*)}\frac{\partial g(E)}{\partial E}\Big|_{E=E^*} \qquad \to \beta = \frac{1}{kT} = \frac{\partial \ln g(E)}{\partial E}\Big|_{E=E^*}$$

$$S = k \ln g \quad \Rightarrow \frac{1}{kT} = \frac{\partial \ln g(E)}{\partial E}\Big|_{E=E^*} \times \left(\frac{k}{k}\right) = \frac{\partial S}{k \partial E}\Big|_{E=E^*} \quad \Rightarrow \frac{1}{T} = \frac{\partial S}{\partial E}\Big|_{E=E^*}$$

$$dU = TdS - PdV + \mu dN \to \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \qquad \Rightarrow E^* = U$$

$$\ln\left[e^{-\beta E} g(E)\right] = \ln\left\{e^{-\beta E} g(E)\right\}\Big|_{E=U} + \frac{\partial \ln\left\{e^{-\beta E} g(E)\right\}}{\partial E}\Big|_{E=U}(E-U) + \frac{1}{2!}\frac{\partial^2 \ln\left\{e^{-\beta E} g(E)\right\}}{\partial E^2}\Big|_{E=U}(E-U)^2 + \cdots$$

$$\frac{\partial \ln\left\{e^{-\beta E} g(E)\right\}}{\partial E}\Big|_{E=U} = \frac{\partial}{\partial E}\left(-\beta E + \ln g(E)\right)_{E=U} = -\beta + \frac{\partial \ln g(E)}{\partial E}\Big|_{E=U}$$

$$-\beta + \frac{\partial S}{k \partial E}\Big|_{E=U} = -\beta + \frac{1}{kT} = 0$$

$$\ln\left[e^{-\beta E} g(E)\right] = -\beta U + \ln g(U) + 0 + \frac{1}{2}\frac{\partial}{\partial E}\frac{\partial}{\partial E}\left(-\beta E + \ln g(E)\right)\Big|_{E=U}(E-U)^2 + \cdots$$

$$\ln\left[e^{-\beta E} g(E)\right] = -\beta U + \frac{S}{k} + \frac{1}{2}\frac{\partial}{\partial E}\left(\frac{1}{kT}\right)(E-U)^2 + \cdots$$

$$= -\beta U + \frac{S}{k} + \frac{1}{2}\frac{\partial \beta}{\partial E}(E-U)^2 + \cdots$$

$$\ln\left[e^{-\beta E} g(E)\right] = -\beta U + \frac{S}{k} - \frac{1}{2}\langle (\Delta E)^2 \rangle^{-1}(E-U)^2 + \cdots$$

$$= -\beta(U - TS) - \frac{1}{2kT^2 C_V}(E-U)^2 + \cdots$$

$$P(E) \propto e^{-\beta E} g(E) \cong e^{-\beta(U-TS)} \cdot \exp\left\{\frac{-(E-U)^2}{2kT^2 C_V}\right\}$$

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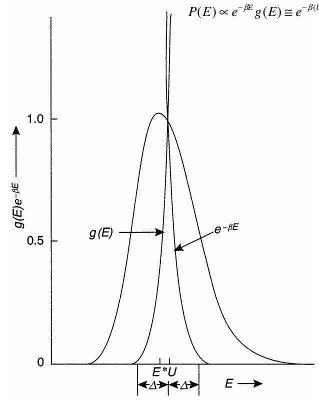

$$g(E)=\begin{cases}\dfrac{V^N}{N!}\left(\dfrac{2\pi m}{h^2}\right)^{3N/2}\dfrac{E^{(3N/2)-1}}{\{(3N/2)-1\}!} & for \quad E\ge 0\\ 0 & for \quad E\le 0\end{cases}$$

$$g(E)=L^{-1}Q(\beta)=\frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty}e^{\beta E}Q(\beta)d\beta$$

$$if \quad N=10 \quad \Rightarrow g(E)e^{-\beta E}\propto E^{(3N/2)-1}\,e^{-\beta E}$$

$$\frac{\partial}{\partial E}\left[g(E)e^{-\beta E}\right]\Big|_{E=E^*}\propto\frac{\partial}{\partial E}\left[E^{(3N/2)-1}\,e^{-\beta E}\right]\Big|_{E=E^*}=0$$

$$\left(\frac{3N}{2}-1\right)E^{*(3N/2)-2}\,e^{-\beta E^*}-\beta e^{-\beta E^*}E^{*(3N/2)-1}=0$$

$$\left(\frac{3N}{2}-1\right)=\beta E^* \quad \to E^*=kT\left(\frac{3N}{2}-1\right) \quad \Rightarrow E^*\sim U=kT\left(\frac{3N}{2}\right)$$

N = 10 $$\frac{E^*}{U}=\frac{\frac{3N}{2}-1}{\frac{3N}{2}}=\frac{\frac{30}{2}-1}{\frac{30}{2}}=\frac{14}{15}$$

$$\sqrt{\left\langle(\Delta E)^2\right\rangle}=\sqrt{(kT^2C_V)}=\sqrt{(kT^2)\left(\frac{3Nk}{2}\right)}=\sqrt{\frac{3N}{2}}\;kT$$

$$U=\frac{3}{2}NkT\to\sqrt{\left\langle(\Delta E)^2\right\rangle}=\sqrt{\frac{3N}{2}}kT\times\left(\frac{3N}{2}\times\frac{2}{3N}\right)=\sqrt{\frac{3N}{2}\times\frac{4}{9N^2}}\;U=\sqrt{\frac{2}{3N}}\;U$$

$$N=10 \quad \to\sqrt{\left\langle(\Delta E)^2\right\rangle}=\sqrt{\frac{2}{30}}\;U=\sqrt{\frac{1}{15}}\;U\approx\sqrt{\frac{1}{16}}\;U=\frac{1}{4}U$$

$$Q_N(V,T)=Lg(E)=\int_0^\infty e^{-\beta E}g(E)dg\cong\int_0^\infty e^{-\beta(U-TS)}\cdot\exp\left\{\frac{-(E-U)^2}{2kT^2C_V}\right\}dE$$

$$=e^{-\beta(U-TS)}\int_0^\infty\exp\left\{\frac{-(E-U)^2}{2kT^2C_V}\right\}dE=e^{-\beta(U-TS)}\sqrt{(2kT^2C_V)}\int_0^\infty e^{-x^2}dx$$

$$=e^{-\beta(U-TS)}\sqrt{(2\pi kT^2C_V)}$$

$$-kT\ln Q_N(V,T)\equiv-kT\left\{-\beta(U-TS)+\ln\sqrt{(2\pi kT^2C_V)}\right\}$$

$$\cong U-TS+\frac{1}{2}\ln\ (2\pi kT^2C_V)=O(N)+O(\ln N)$$

$$A\approx U-TS$$

$$\left\langle x_i\frac{\partial H}{\partial x_j}\right\rangle=?$$

$$\left\langle x_i\frac{\partial H}{\partial x_j}\right\rangle=\frac{\int\left(x_i\frac{\partial H}{\partial x_j}\right)e^{-\beta H}d\omega}{\int e^{-\beta H}d\omega}$$

$$d\omega=d^{3N}qd^{3N}p$$

$$I=\int\left(x_i\frac{\partial H}{\partial x_j}\right)e^{-\beta H}d\omega$$

$$\left(\frac{\partial}{\partial x_j}\right)\left(x_ie^{-\beta H}\right)=\frac{\partial x_i}{\partial x_j}e^{-\beta H}+x_i\frac{\partial}{\partial x_j}e^{-\beta H}$$

$$\frac{\partial}{\partial x_j}e^{-\beta H}=\frac{\partial}{\partial H}e^{-\beta H}\frac{\partial H}{\partial x_j}=-\beta e^{-\beta H}\frac{\partial H}{\partial x_j}$$

$$\left(\frac{\partial}{\partial x_j}\right)\left(x_ie^{-\beta H}\right)=\delta_{ij}e^{-\beta H}+x_i(-\beta)\frac{\partial H}{\partial x_j}e^{-\beta H}$$

$$x_i\frac{\partial H}{\partial x_j}e^{-\beta H}=\frac{1}{\beta}\left[-\frac{\partial}{\partial x_j}\ \left(x_ie^{-\beta H}\right)+\delta_{ij}e^{-\beta H}\right]$$

$$I=\int\frac{1}{\beta}\left[-\frac{\partial}{\partial x_j}\left(x_ie^{-\beta H}\right)+\delta_{ij}e^{-\beta H}\right]d\omega \qquad d\omega=dx_idx_j$$

$$=\int-\frac{1}{\beta}x_ie^{-\beta H}\Big|_{(x_j)_1}^{(x_j)_2}d\omega^{(j)}+\frac{1}{\beta}\int\delta_{ij}e^{-\beta H}d\omega$$

$$=0+kT\delta_{ij}\int e^{-\beta H}d\omega \qquad d\omega^{(j)}\equiv\frac{d\omega}{dx_j}\equiv dx_i$$

$$=kT\delta_{ij}\int e^{-\beta H}d\omega$$

$$\left\langle x_i\frac{\partial H}{\partial x_j}\right\rangle=\delta_{ij}kT$$

# A system of harmonic oscillators

We shall now examine a system of $N$, practically independent, harmonic oscillators. This study will not only provide an interesting illustration of the canonical ensemble formulation but will also serve as a basis for some of our subsequent studies in this text. Two important problems in this line are (i) the theory of the black-body radiation (or the "statistical mechanics of photons") and (ii) the theory of lattice vibrations (or the "statistical mechanics of phonons"); see Secs 7.2 and 7.3 for details.

We start with the specialized situation when the oscillators can be treated *classically*. The Hamiltonian of any one of them (assumed to be one-dimensional) is then given by

$$H(q_i,p_i)=\frac{1}{2}m\omega^2q_i^2+\frac{1}{2m}p_i^2 \qquad (i=1,\ldots,N)$$

$$Q_1(\beta)=\frac{1}{h}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}e^{-\beta H(q,p)}\,dq\,dp$$

$$=\frac{1}{h}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\exp\left\{-\beta\left(\frac{1}{2}m\omega^2q^2+\frac{1}{2m}p^2\right)\right\}dq\,dp$$

$$=\frac{1}{h}\left(\frac{2\pi}{\beta m\omega^2}\right)^{1/2}\left(\frac{2\pi m}{\beta}\right)^{1/2}=\frac{1}{\beta\hbar\omega}$$

$$Q_N(\beta) = [Q_1(\beta)]^N = (\beta\hbar\omega)^{-N}$$

note that in writing (3) we have assumed the oscillators to be *distinguishable*. This is so because, as we shall see later, these oscillators are merely a representation of the energy levels available in the system; they are not particles (or even "quasi-particles"). It is actually photons in one case and phonons in the other, which distribute themselves over the various oscillator levels, that are *indistinguishable*!

$$Q_N(\beta) = [Q_1(\beta)]^N = (\beta\hbar\omega)^{-N}$$

$$A \equiv -kT \ln Q_N(\beta) =$$

$$= -kT \ln(\beta\hbar\omega)^{-N} =$$

$$= NkT \ln\left(\frac{\hbar\omega}{kT}\right)$$

$$dA = -SdT - PdV + \mu dN$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \frac{A}{N} = kT \ln\left(\frac{\hbar\omega}{kT}\right)$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = 0$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = -Nk \ln\left(\frac{\hbar\omega}{kT}\right) + Nk$$

$$= Nk\left[-\ln\left(\frac{\hbar\omega}{kT}\right) + 1\right]$$

$$U = A + TS = NkT$$

$$C_P = C_V = Nk$$

$$g(E) = L^{-1}Q_N(\beta) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} Q_N(\beta)\, e^{\beta E} d\beta$$

$$= \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} (\beta\hbar\omega)^{-N} e^{\beta E} d\beta$$

$$= \frac{1}{(\hbar\omega)^N}\frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} \frac{e^{\beta E}}{\beta^N}\, d\beta \qquad (\beta' > 0)$$

$$= \begin{cases} \dfrac{1}{(\hbar\omega)^N}\dfrac{E^{N-1}}{(N-1)!} & for \quad E \geq 0 \\ 0 & for \quad E \leq 0 \end{cases}$$

$$S(N,E) = k \ln g(E) \approx k \ln\left[\frac{1}{(\hbar\omega)^N}\frac{E^N}{N!}\right]$$

$$= k\left[\ln\left(\frac{E}{\hbar\omega}\right)^N - \ln N!\right] \approx k\left[N \ln\left(\frac{E}{\hbar\omega}\right) - N\ln N + N\right]$$

We note that the mean energy per oscillator is in complete agreement with the equipartition theorem, namely $2 \times \frac{1}{2}kT$, for we have here *two* independent quadratic terms in the single-oscillator Hamiltonian.

$$S(N,E) = k\left[N \ln\left(\frac{E}{N\hbar\omega}\right) + N\right]$$

$$= Nk\left[\ln\left(\frac{E}{N\hbar\omega}\right) + 1\right]$$

$$dE = TdS - PdV + \mu dN$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{Nk}{E} \Rightarrow \qquad E = NkT$$

$$S(N,E) = Nk\left[\ln\left(\frac{kT}{\hbar\omega}\right) + 1\right]$$

We now take up the quantum-mechanical situation, according to which the energy eigenvalues of a one-dimensional harmonic oscillator are given by

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad (n = 0,\ 1,\ 2, \ldots)$$

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$$Q_1(\beta) = \sum_{n=0}^{\infty} e^{-\beta\varepsilon_n} = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega}$$

$$= e^{-(1/2)\hbar\beta\omega} + e^{-(3/2)\hbar\beta\omega} + e^{-(5/2)\hbar\beta\omega} + \cdots$$

$$= e^{-(1/2)\hbar\beta\omega}\left\{1 + e^{-\hbar\beta\omega} + e^{-2\hbar\beta\omega} + \cdots\right\}$$

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

$$= \frac{\exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1 - \exp(-\beta\hbar\omega)} \times \frac{\exp\left(\frac{1}{2}\beta\hbar\omega\right)}{\exp\left(\frac{1}{2}\beta\hbar\omega\right)}$$

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

$$Q_1(\beta) = \left\{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right\}^{-1}$$

$$Q_N(\beta) = [Q_1(\beta)]^N = \left[2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right]^{-N}$$

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

$$A = -kT \ln Q_N(\beta) = NkT \ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right]$$

$$= N\left[\frac{1}{2}\hbar\omega + kT\ln\left\{1 - e^{-\beta\hbar\omega}\right\}\right]$$

$$dA = -SdT - PdV + \mu dN$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \frac{A}{N} = \left[\frac{1}{2}\hbar\omega + kT\ln\left\{1 - e^{-\beta\hbar\omega}\right\}\right]$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = 0$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = Nk\left[\frac{1}{2}\beta\hbar\omega\, \coth\left(\frac{1}{2}\beta\hbar\omega\right) - \ln\left\{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right\}\right]$$

$$= Nk\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln\left\{1 - e^{-\beta\hbar\omega}\right\}\right]$$

$$U = A + TS = -\frac{\partial \ln Q_N(\beta)}{\partial\beta}$$

$$= \frac{1}{2}N\hbar\omega\, \coth\left(\frac{1}{2}\beta\hbar\omega\right)$$

$$= N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right]$$

$$C_P = C_V = \left(\frac{\partial U}{\partial T}\right) = Nk\left(\frac{1}{2}\beta\hbar\omega\right)^2 \operatorname{cosech}^2\left(\frac{1}{2}\beta\hbar\omega\right)$$

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

Formula (20) is especially significant, for it shows that the quantum-mechanical oscillators do not obey the equipartition theorem. The mean energy per oscillator is different from the equipartition value $kT$; actually, it is always greater than $kT$; see curve 2 in Fig. 3.4. Only in the limit of high temperatures, where the thermal energy $kT$ is much larger than the energy quantum $\hbar\omega$, does the mean energy per oscillator tend to the equipartition value. It should be noted here that if the zero-

[redacted]

$$U = N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]$$

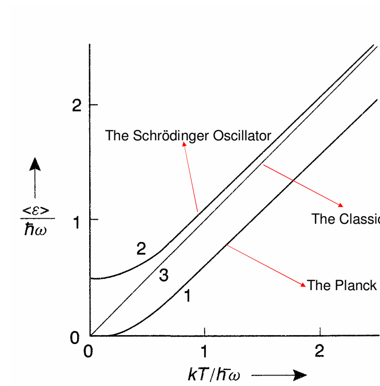
$$\approx N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{1+\beta\hbar\omega+\frac{1}{2}(\beta\hbar\omega)^2-1}\right] = N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\beta\hbar\omega+\frac{1}{2}(\beta\hbar\omega)^2}\right]$$

$$= N\left[\frac{1}{2}\hbar\omega + \frac{1}{\beta}\frac{1}{1+\frac{1}{2}\beta\hbar\omega}\right] \approx N\left[\frac{1}{2}\hbar\omega + \frac{1}{\beta}\left(1-\frac{1}{2}\beta\hbar\omega\right)\right]$$

$$= N\left[\frac{1}{2}\hbar\omega + \frac{1}{\beta} - \frac{1}{2}\hbar\omega\right] = N\,\frac{1}{\beta} = NkT$$

[redacted]

oscillator tend to the equipartition value. It should be noted here that if the zero-point energy $\frac{1}{2}\hbar\omega$ were not present, the limiting value of the mean energy would be $(kT - \frac{1}{2}\hbar\omega)$, and not $kT$ – we may call such an oscillator the *Planck oscillator*; see curve 1 in the figure. In passing, we observe that the specific heat (21), which is the same for the Planck oscillator as for the Schrödinger oscillator, is temperature-dependent; moreover, it is always less than, and at high temperatures tends to, the classical value (9).




Indeed, for $kT \gg \hbar\omega$, formulae (14)–(21) go over to their classical counterparts, namely (2)–(9), respectively.

**تمرین: درستی عبارت فوق را تحقیق کنید.**

We shall now determine the density of states $g(E)$ of the $N$-oscillator system from its partition function (15). Carrying out the binomial expansion of this expression, we have

$$Q_N(\beta) = e^{-(N/2)\beta\hbar\omega}\left[1-e^{-\beta\hbar\omega}\right]^{-N}$$

Then we can find the partition function. It is:

$$g(E) = \sum_{R=0}^{\infty}\binom{N+R-1}{R}\,\delta\left(E-\left\{R+\frac{1}{2}N\right\}\hbar\omega\right)$$

Why is the above function the density of state for the given partition function?

$$f(x) = (1-x)^{-N}$$

$$f(x) = f(0) + f'(0)x + \frac{f^{(2)}(0)}{2!}x^2 + \frac{f^{(3)}(0)}{3!}x^3 + \frac{f^{(4)}(0)}{4!}x^4 + \cdots$$

$$\begin{cases} f'(x) = N(1-x)^{-N-1} & \to f'(0) = N \\ f^{(2)}(x) = N(N+1)(1-x)^{-N-2} & \to f^{(2)}(0) = N(N+1) \\ f^{(3)}(x) = N(N+1)(N+2)(1-x)^{-N-3} & \to f^{(3)}(0) = N(N+1)(N+2) \\ f^{(4)}(x) = N(N+1)(N+2)(N+3)(1-x)^{-N-4} & \to f^{(4)}(0) = N(N+1)(N+2)(N+3) \\ \vdots & \end{cases}$$

$$f(x) = 1 + N\ x + \frac{N(N+1)}{2!}x^2 + \frac{N(N+1)(N+2)}{3!}x^3 + \frac{N(N+1)(N+2)(N+3)}{4!}x^4 + \cdots$$

$$f(x) = 1 + N\ x + \frac{N(N+1)}{2!}x^2 + \frac{N(N+1)(N+2)}{3!}x^3 + \frac{N(N+1)(N+2)(N+3)}{4!}x^4 + \cdots$$

$$f(x) = \sum_{R=0}^{\infty} \binom{N+R-1}{R} x^R$$

$$= \frac{(N+0-1)!}{0!(N-1)!}x^0 + \frac{N!}{1!(N-1)!}x + \frac{(N+1)!}{2!(N-1)!}x^2 + \frac{(N+2)!}{3!(N-1)!}x^3 + \frac{(N+3)!}{4!(N-1)!}x^4 + \cdots$$

$$= 1 + Nx + \frac{(N+1)N}{2!}x^2 + \frac{(N+2)(N+1)N}{3!}x^3 + \frac{(N+3)(N+2)(N+1)N}{4!}x^3 + \cdots$$ ☺

$$Q_N(\beta) = e^{-(N/2)\beta\hbar\omega}\left[1-e^{-\beta\hbar\omega}\right]^{-N} = e^{-(N/2)\beta\hbar\omega}\sum_{R=0}^{\infty}\binom{N+R-1}{R}\left(e^{-\beta\hbar\omega}\right)^R$$

$$= e^{-(N/2)\beta\hbar\omega}\sum_{R=0}^{\infty}\binom{N+R-1}{R}\left(e^{-\beta\hbar\omega}\right)^R$$

$$= \sum_{R=0}^{\infty}\binom{N+R-1}{R} e^{-\beta\left(\frac{1}{2}N\hbar\omega + R\hbar\omega\right)} = \sum_{R=0}^{\infty}\binom{N+R-1}{R} e^{-\beta\hbar\omega\left(\frac{1}{2}N+R\right)}$$

$$Q_N(V,T) = \sum_{R=0}^{\infty}\binom{N+R-1}{R} e^{-\beta\hbar\omega\left(\frac{1}{2}N+R\right)}$$

Comparing this with the formula $Q_N(\beta) = \int_0^{\infty} g(E)\ e^{-\beta E} dE = L\, g(E)$

We conclude that

$$g(E) = \sum_{R=0}^{\infty}\binom{N+R-1}{R}\ \delta\left(E - \left\{R + \frac{1}{2}N\right\}\hbar\omega\right)$$

Because

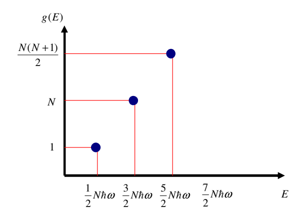
$$Q_N(\beta) = \int_0^{\infty}\sum_{R=0}^{\infty}\binom{N+R-1}{R}\ \delta\left(E - \left\{R + \frac{1}{2}N\right\}\hbar\omega\right)e^{-\beta E}dE$$

$$= \sum_{R=0}^{\infty}\int_0^{\infty}\binom{N+R-1}{R}\delta\left(E - \left\{R + \frac{1}{2}N\right\}\hbar\omega\right)e^{-\beta E}dE$$

$$= \sum_{R=0}^{\infty}\binom{N+R-1}{R} e^{-\beta\left(\left\{R+\frac{1}{2}N\right\}\hbar\omega\right)}$$ ☺

$$g(E) = \sum_{R=0}^{\infty}\binom{N+R-1}{R}\ \delta\left(E - \left\{R + \frac{1}{2}N\right\}\hbar\omega\right)$$

where $\delta(x)$ denotes the Dirac delta function. Equation (23) implies that there are $(N+R-1)!/R!(N-1)!$ microstates available to the system when its energy $E$ has the discrete value $(R+\frac{1}{2}N)\hbar\omega$, where $R = 0, 1, 2, \ldots$, and that no microstate is available for other values of $E$. This is hardly surprising, but it is instructive to look at this result from a slightly different point of view.

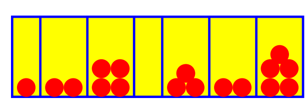



This is hardly surprising, but it is instructive to look at this result from a slightly different point of view.

We consider the following problem which arises naturally in the microcanonical ensemble theory. Given an energy $E$ for distribution among a set of $N$ harmonic oscillators, each of which can be in any one of the eigenstates (13), what is the total number of *distinct* ways in which the process of distribution can be carried out? Now, in view of the form of the eigenvalues $\varepsilon_n$, it makes sense to give away, right in the beginning, the zero-point energy $\frac{1}{2}\hbar\omega$ to each of the $N$ oscillators and convert the rest of it into quanta (of energy $\hbar\omega$). Let $R$ be the number of these quanta; then

$$R = \frac{\left(E - \frac{1}{2}N\hbar\omega\right)}{\hbar\omega}$$

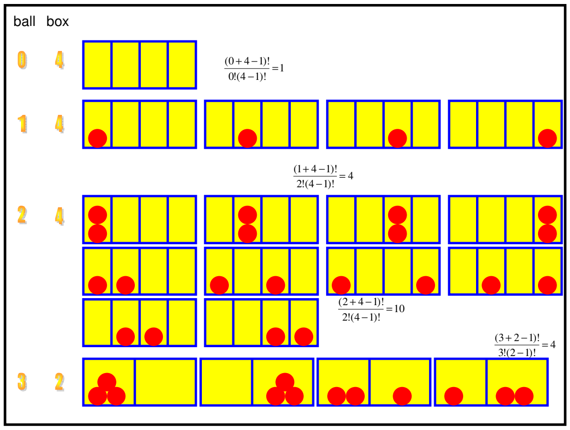
Number of ways to put 17 indistinguishable balls in 7 distinguishable boxes



$$\frac{23!}{17!6!}$$

Clearly, $R$ must be an integer; by implication, $E$ must be of the form $(R+\frac{1}{2}N)\hbar\omega$. The problem then reduces to determining the number of *distinct* ways of allotting $R$ quanta to $N$ oscillators, such that an oscillator may have 0 or 1 or 2 ... quanta; in other words, we have to determine the number of *distinct* ways of putting $R$ *indistinguishable* balls into $N$ *distinguishable* boxes, such that a box may receive 0 or 1 or 2 ... balls. A little reflection will show that this is precisely the number of permutations that can be realized by shuffling $R$ balls, placed along a row, with $(N-1)$ partitioning lines (that divide the given space into $N$ boxes); see Fig. 3.5. The answer clearly is

$$\frac{(R+N-1)!}{R!(N-1)!}$$




We can determine the entropy of the system from the number (25). Since $N \gg 1$, we have

$$S = k\ \ln\left\{\binom{N+R-1}{R}\right\} = k\ \ln\frac{(N+R-1)!}{R!(N-1)!}$$

$$\approx k\ \ln\frac{(N+R)!}{R!N!} = k\ \{\ln(N+R)! - \ln R! - \ln N!\}$$

$$\approx k\ \{(N+R)\ln(N+R) - (N+R) - R\ln R + R - N\ln N + N\}$$

the number $R$ is, of course, a measure of the energy of the system, see (24). For the temperature of the system, we obtain

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \left(\frac{\partial S}{\partial R}\right)_N \left(\frac{\partial R}{\partial E}\right)_N$$

$$R = \frac{E - \frac{1}{2}\hbar\omega}{\hbar\omega} \quad \Rightarrow E = (R + N/2)\hbar\omega \quad \Longrightarrow \quad \frac{\partial E}{\partial R} = \hbar\omega$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \left(\frac{\partial S}{\partial R}\right)_N \left(\frac{\partial R}{\partial E}\right)_N = \frac{1}{\hbar\omega}\left(\frac{\partial S}{\partial R}\right)_N$$

$$S \approx k\ \{(N+R)\ln(N+R) - (N+R) - R\ln R + R - N\ln N + N\}$$

$$S \approx k\ \{(N+R)\ln(N+R) - R\ln R - N\ln N\}$$

$$\frac{1}{T} = \frac{k}{\hbar\omega}\left\{\ln(N+R) + (N+R)\frac{1}{(N+R)} - \ln R - R\frac{1}{R}\right\} = \frac{k}{\hbar\omega}\{\ln(N+R) - \ln R\}$$

$$= \frac{k}{\hbar\omega}\ln\left(\frac{R+N}{R}\right) = \frac{k}{\hbar\omega}\ln\left(\frac{E + \frac{1}{2}N\hbar\omega}{E - \frac{1}{2}N\hbar\omega}\right) \quad \Longrightarrow \quad \ln\left(\frac{E + \frac{1}{2}N\hbar\omega}{E - \frac{1}{2}N\hbar\omega}\right) = \frac{\hbar\omega}{kT}$$

$$\frac{E + \frac{1}{2}N\hbar\omega}{E - \frac{1}{2}N\hbar\omega} = \exp\left[\frac{\hbar\omega}{kT}\right] \quad \Longrightarrow \quad E\left(1 - \exp\left[\frac{\hbar\omega}{kT}\right]\right) = -\frac{1}{2}N\hbar\omega \times \left(1 + \exp\left[\frac{\hbar\omega}{kT}\right]\right)$$

$$E = \frac{1}{2}N\hbar\omega \times \frac{\exp(\beta\hbar\omega) + 1}{\exp(\beta\hbar\omega) - 1}$$

$$E = \frac{1}{2}N\hbar\omega \times \frac{\exp(\beta\hbar\omega) + 1}{\exp(\beta\hbar\omega) - 1}$$

Which is identical with

$$U = N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right] = N\frac{1}{2}\hbar\omega\left[1 + \frac{2}{e^{\beta\hbar\omega} - 1}\right] = \frac{N}{2}\hbar\omega\left[\frac{e^{\beta\hbar\omega} - 1 + 2}{e^{\beta\hbar\omega} - 1}\right]$$

It can be further checked that, by eliminating $R$ between (26) and (27), we obtain precisely the formula (19) for $S(N, T)$. Thus, once again, we find that the results obtained by following the microcanonical approach and the canonical approach are asymptotically the same.

$$S \approx k\ \{(N+R)\ln(N+R) - R\ln R - N\ln N\}$$

$$\frac{1}{T} = \frac{k}{\hbar\omega}\ln\left(\frac{R+N}{R}\right) \quad \Longrightarrow \quad S = Nk\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln\left\{1 - e^{-\beta\hbar\omega}\right\}\right]$$

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Finally, we may consider the classical limit when $E/N$, the mean energy per oscillator, is much larger than the energy quantum $\hbar\omega$, i.e. when $R \gg N$. The expression (25) may, in that case, be replaced by

$$\binom{N+R-1}{R} = \frac{(N+R-1)!}{R!(N-1)!} \qquad R = \frac{E - \frac{1}{2}N\hbar\omega}{\hbar\omega} \approx \frac{E}{\hbar\omega}$$

$$= \frac{(N+R-1)(N+R-2)\cdots(R+1)}{(N-1)!} \approx \frac{R^{N-1}}{(N-1)!} = \frac{E^{N-1}}{(\hbar\omega)^{N-1}(N-1)!}$$

$$S \approx k\{N\ln(R/N) + N\} \approx Nk\left\{\ln\left(\frac{E}{N\hbar\omega}\right) + 1\right\}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N \approx \frac{Nk}{E}$$

$$\frac{E}{N} \approx kT$$