by (12). This proves that

$$\boxed{F = -\tau \log Z} \tag{55}$$

satisfies the required differential equation (52).

It would appear possible for F/τ to contain an additive constant α such that $F = -\tau \log Z + \alpha\tau$. However, the entropy must reduce to $\log g_0$ when the temperature is so low that only the g_0 coincident states at the lowest energy ε_0 are occupied. In that limit $\log Z \to \log g_0 - \varepsilon_0/\tau$, so that $\sigma = -\partial F/\partial\tau \to \partial(\tau \log Z)/\partial\tau = \log g_0$ only if $\alpha = 0$.

We may write the result as

$$Z = \exp(-F/\tau); \tag{56}$$

and the Boltzmann factor (11) for the occupancy probability of a quantum state s becomes

$$P(\varepsilon_s) = \frac{\exp(-\varepsilon_s/\tau)}{Z} = \exp[(F - \varepsilon_s)/\tau]. \tag{57}$$

IDEAL GAS: A FIRST LOOK

One atom in a box. We calculate the partition function Z_1 of one atom of mass M free to move in a cubical box of volume $V = L^3$. The orbitals of the free particle wave equation $-(\hbar^2/2M)\nabla^2\psi = \varepsilon\psi$ are

$$\psi(x,y,z) = A \sin(n_x \pi x/L) \sin(n_y \pi y/L) \sin(n_z \pi z/L)\ , \tag{58}$$

where n_x, n_y, n_z are any positive integers, as in Chapter 1. Negative integers do not give independent orbitals, and a zero does not give a solution. The energy values are

$$\varepsilon_n = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 ({n_x}^2 + {n_y}^2 + {n_z}^2). \tag{59}$$

We neglect the spin and all other structure of the atom, so that a state of the system is entirely specified by the values of n_x, n_y, n_z.