

product $g_1 g_2$ is reduced to $e^{-400} \approx 10^{-174}$ of its maximum value. This is an extremely large reduction, so that $g_1 g_2$ is truly a very sharply peaked function of s_1 . The probability that the fractional deviation will be 10^{-10} or larger is found by integrating (17) from $\delta = 10^{12}$ out to a value of the order of s or of N , thereby including the area under the wings of the probability distribution. This is the subject of Problem 6. An upper limit to the integrated probability is given by $N \times 10^{-174} = 10^{-152}$, still very small. When two systems are in thermal contact, the values of s_1, s_2 that occur most often will be very close to the values of \hat{s}_1, \hat{s}_2 for which the product $g_1 g_2$ is a maximum. It is extremely rare to find systems with values of s_1, s_2 perceptibly different from \hat{s}_1, \hat{s}_2 .

What does it mean to say that the probability of finding the system with a fractional deviation larger than $\delta/N_1 = 10^{-10}$ is only 10^{-152} of the probability of finding the system in equilibrium? We mean that the system will never be found with a deviation as much as 1 part in 10^{10} , small as this deviation seems. We would have to sample 10^{152} similar systems to have a reasonable chance of success in such an experiment. If we sample one system every 10^{-12} s, which is pretty fast work, we would have to sample for 10^{140} s. The age of the universe is only 10^{18} s. Therefore we say with great surety that the deviation described will never be observed. The estimate is rough, but the message is correct. The quotation from Boltzmann given at the beginning of this chapter is relevant here.

We may expect to observe substantial fractional deviations only in the properties of a *small* system in thermal contact with a large system or reservoir. The energy of a small system, say a system of 10 spins, in thermal contact with a large reservoir may undergo fluctuations that are large in a fractional sense, as have been observed in experiments on the Brownian motion of small particles in suspension in liquids. The average energy of a small system in contact with a large system can always be determined accurately by observations at one time on a large number of identical small systems or by observations on one small system over a long period of time.

THERMAL EQUILIBRIUM

The result for the number of accessible states of two model spin systems in thermal contact may be generalized to any two systems in thermal contact, with constant total energy $U = U_1 + U_2$. By direct extension of the earlier argument, the multiplicity $g(N, U)$ of the combined system is:

$$g(N, U) = \sum_{U_1} g_1(N_1, U_1) g_2(N_2, U - U_1) , \quad (18)$$

summed over all values of $U_1 \leq U$. Here $g_1(N_1, U_1)$ is the number of accessible states of system 1 at energy U_1 . A configuration of the combined system is specified by the value of U_1 , together with the constants U, N_1, N_2 . The number of accessible states in a configuration is the product $g_1(N_1, U_1) g_2(N_2, U - U_1)$. The sum over all configurations gives $g(N, U)$.