This may be rearranged to give

$$\boxed{dU = \tau d\sigma - pdV + \mu dN\ ,} \tag{39}$$

which is a broader statement of the thermodynamic identity than we were able to develop in Chapter 3.

GIBBS FACTOR AND GIBBS SUM

The Boltzmann factor, derived in Chapter 3, allows us to give the ratio of the probability that a system will be in a state of energy ε_1 to the probability the system will be in a state of energy ε_2, for a system in thermal contact with a reservoir at temperature τ:

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}. \tag{40}$$

This is perhaps the best known result of statistical mechanics. The Gibbs factor is the generalization of the Boltzmann factor to a system in thermal and diffusive contact with a reservoir at temperature τ and chemical potential μ. The argument retraces much of that presented in Chapter 3.

We consider a very large body with constant energy U_0 and constant particle number N_0. The body is composed of two parts, the very large reservoir $\mathcal{R}$ and the system $\mathcal{S}$, in thermal and diffusive contact (Figure 5.8). They may exchange particles and energy. The contact assures that the temperature and the chemical potential of the system are equal to those of the reservoir. When the system has N particles, the reservoir has $N_0 - N$ particles; when the system has energy ε, the reservoir has energy $U_0 - \varepsilon$. To obtain the statistical properties of the system, we make observations as before on identical copies of the system + reservoir, one copy for each accessible quantum state of the combination. What is the probability in a given observation that the system will be found to contain N particles and to be in a state s of energy ε_s?

The state s is a state of a system having some specified number of particles. The energy $\varepsilon_{s(N)}$ is the energy of the state s of the N-particle system; sometimes we write only ε_s, if the meaning is clear. When can we write the energy of a system having N particles in an orbital as N times the energy of one particle in the orbital? Only when interactions between the particles are neglected, so that the particles may be treated as independent of each other.