Totally macroscopic application of the second law requires that we be able to determine entropy change on a purely macroscopic basis. We obtain this by combining the energy conservation principle with the equilibrium distribution function developed above.

On a microscopic basis the internal energy of a system is $U = \sum_j n_{j,i}\varepsilon_j(V)$. Our previous development concerned isolated systems. The principal means by which closed system states are altered are through heat and/or work interactions. The relationship between internal energy, heat, and work is the intrinsic first law. Since our development is in terms of simple compressible media $[\varepsilon_j = \varepsilon_j(V)]$, we employ eqn. IB-16c.

$$dU = \sum_j \varepsilon_j(V)\delta n_{j,i} + \sum_j \left(n_{j,i}\frac{d\varepsilon_j(V)}{dV}\right) dV = \left(đQ + đW^i_{irr}\right) - p\,dV$$

Processes that occur at constant volume must satisfy the condition

$$đQ + đW^i_{irr} = \sum_j \varepsilon_j(V)\delta n_{j,i} \qquad \text{(IIIB-18)}$$

Such energy addition processes do not affect the magnitude of the levels, $[d\varepsilon_j(V) = 0]$, rather they shift particles from lower into higher energy levels. The volume change is independent of eqn. IIIB-18; therefore, the terms in dV are also separately equal.[15]

$$đW^i_{rev,c} = -\,p\,dV = \sum_j \left(n_{j,i}\frac{d\varepsilon_j(V)}{dV}\right) dV = \sum_j n_{j,i}d\varepsilon_j(V) \qquad \text{(IIIB-19)}$$

This relationship developed for simple compressible media is valid for other simple and complex media as well

$$đW^i_{rev} = \sum_j n_{j,i}d\varepsilon_j(V) \qquad \text{(IIIB-19)}$$

Thus, if a reversible work interaction occurs to a system in equilibrium $(n_{j,i} = n_{j,eq})$ the system remains in equilibrium during the process $(\delta n_{j,i} = 0)$. The energy is altered exclusively by the change in the level magnitudes. If heat or irreversible work interaction occurs the system must re-equilibrate to new equilibrium states after each energy addition. Thus rapid heat and/or irreversible work processes tend to leave the system in nonequilibrium states.

Example 4. The 10^4 distinguishable particles of a fictitious, but illustrative, system are distributed among two levels ($\varepsilon_1 = 0$, $g_1 = 5 \cdot 10^2$; $\varepsilon_2 = 6.90 \cdot 10^{-21}$ J/part, $g_2 = 10^3$). The system is in equilibrium and its total energy is $U = 2.07 \cdot 10^{-17}$ J. (a) Determine the temperature and entropy of the system in this equilibrium state. (b) Reversible (cont'd)

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[15]This relationship also gives us the true microscopic meaning of pressure, as opposed to the "pseudopressure" of Unit IIIA,

$$p_{j,i} = -\,n_{j,i}\frac{d\varepsilon_j(V)}{dV}\,; \qquad p_i = \sum_j n_{j,i}\frac{d\varepsilon_j(V)}{dV}\,; \qquad p_{eq} = \sum_j n_{j,eq}\frac{d\varepsilon_j(V)}{dV}$$