

1.2: The 2nd law of thermodynamics, entropy, and temperature

Thermodynamics accepts a phenomenological approach to the entropy S , postulating that there is such a unique extensive measure of the aggregate disorder, and that in a *closed system* (defined as a system completely isolated from its environment, i.e. the system with its internal energy fixed) it may only grow in time, reaching its constant (maximum) value at equilibrium:¹⁵

2nd law of thermodynamics:

$$\boxed{dS \geq 0.} \quad (1.2.1)$$

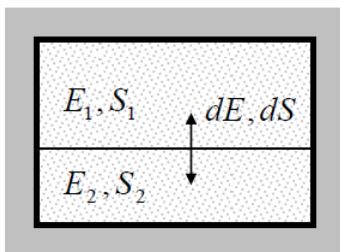


Figure 1.2.1: A composite thermodynamic system.

Neglecting the energy of interaction between the parts (which is always possible at $N \gg 1$, and in the absence of long-range interactions), we may use the extensive character of the variables E and S to write

$$E = E_1(S_1) + E_2(S_2), \quad S = S_1 + S_2, \quad (1.2.2)$$

for the full energy and entropy of the system. Now let us use them to calculate the following derivative:

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_1} \equiv \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{dE_2}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{d(E - E_1)}{dE_1}. \quad (1.2.3)$$

Since the total energy E of the closed system is fixed and hence independent of its re-distribution between the subsystems, we have to take $dE/dE_1 = 0$, and Equation (1.2.3) yields

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \quad (1.2.4)$$

According to the 2nd law of thermodynamics, when the two parts have reached the thermodynamic equilibrium, the total entropy S reaches its maximum, so that $dS/dE_1 = 0$, and Equation (1.2.4) yields

$$\frac{dS_1}{dE_1} = \frac{dS_2}{dE_2} \quad (1.2.5)$$

This equality shows that if a thermodynamic system may be partitioned into weakly interacting macroscopic parts, their derivatives dS/dE should be equal in the equilibrium. The reciprocal of this derivative is called *temperature*. Taking into account that our analysis pertains to the situation (Figure 1.2.1) when both volumes $V_{1,2}$ are fixed, we may write this definition as

Definition of Temperature

$$\boxed{\left(\frac{\partial E}{\partial S} \right)_V \equiv T,} \quad (1.2.6)$$

the subscript V meaning that volume is kept constant at the differentiation. (Such notation is common and very useful in thermodynamics, with its broad range of variables.)

In those units, the entropy becomes dimensional: $S_K = k_B S$.

- according to Equation (1.2.6), the temperature is an intensive variable (since both E and S are extensive), i.e., in a system of similar particles, it is independent of the particle number N ;
- temperatures of all parts of a system are equal at equilibrium – see Equation (1.2.5);

iii. in a closed system whose parts are *not* in equilibrium, thermal energy (*heat*) always flows from a warmer part (with higher T) to the colder part.

In order to prove the last property, let us revisit the closed, composite system shown in Figure 1.2.1, and consider another derivative:

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt} \equiv \frac{dS_1}{dE_1} + \frac{dE_1}{dt} + \frac{dS_2}{dE_2} \frac{dE_2}{dt}. \quad (1.2.7)$$

If the internal state of each part is very close to equilibrium (as was assumed from the very beginning) at each moment of time, we can use Equation (1.2.6) to replace the derivatives $dS_{1,2}/dE_{1,2}$ with $1/T_{1,2}$, getting

$$\frac{dS}{dt} = \frac{1}{T_1} \frac{dE_1}{dt} + \frac{1}{T_2} \frac{dE_2}{dt} \quad (1.2.8)$$

Since in a closed system $E = E_1 + E_2 = \text{const}$, these time derivatives are related as $dE_2/dt = -dE_1/dt$, and Equation (1.2.8) yields

$$\frac{dS}{dt} - \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt} \quad (1.2.9)$$

But according to the 2nd law of thermodynamics, this derivative cannot be negative: $dS/dt \geq 0$. Hence,

$$\left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt} \geq 0 \quad (1.2.10)$$

For example, if $T_1 > T_2$, then $dE_1/dt \leq 0$, i.e. the warmer part gives energy to its colder counterpart.

Note also that at such a heat exchange, at fixed volumes $V_{1,2}$, and $T_1 \neq T_2$, increases the total system's entropy, without performing any "useful" mechanical work – see Equation (1.1.1).

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