1.3 Thermodynamic Potentials

The term thermodynamic potential derives from an analogy with mechanical potential energy. In certain circumstances the work obtainable from a macroscopic system is related to the change in the appropriately defined thermodynamic potential. The simplest example is the internal energy $E(S,V)$ for a PVT system. The second law for reversible processes reads

$$dE = TdS - PdV = đQ - đW \ . \tag{1.21}$$

In a reversible adiabatic transformation the decrease in internal energy is equal to the amount of work done by the expanding system. If the transformation is adiabatic but not reversible, $đQ = 0$ and the first law yields

$$\Delta E = -(\Delta W)_{irrev} \tag{1.22}$$

with the same change in E as in a reversible transformation connecting the same endpoints in the thermodynamic space. However, the change in entropy is not necessarily zero and must be calculated along a reversible path:

$$\Delta E = (\Delta Q)_{rev} - (\Delta W)_{rev} \ . \tag{1.23}$$

Subtracting and using $(đQ)_{rev} = TdS$, we find that

$$(\Delta W)_{rev} - (\Delta W)_{irrev} = \int TdS \geq 0 \ . \tag{1.24}$$

Thus the decrease in internal energy is equal to the maximum amount of work obtainable through an adiabatic process, and this maximum is achieved if the process is reversible.

We now generalize the formulation to allow other forms of work, as well as the exchange of particles between the system under consideration and its surroundings. This more general internal energy is a function of the entropy, the extensive generalized displacements, and the number of particles of each species: $E = E(S, \{x_i\}, \{N_j\})$ with a differential (for reversible processes)

$$dE = TdS + \sum_i X_i dx_i + \sum_j \mu_j dN_j \ . \tag{1.25}$$

Here N_j is the number of molecules of type j and the *chemical potential* μ_j is defined by (1.25). We are now in a position to introduce a number of other useful thermodynamic potentials. The *Helmholtz free energy*, A, is related to the internal energy through a *Legendre transformation*:

$$A = E - TS \ . \tag{1.26}$$

The quantity A is a state function with differential

$$\begin{aligned} dA &= dE - TdS - SdT \\ &= -SdT + \sum_i X_i dx_i + \sum_j \mu_j dN_j \ . \end{aligned} \tag{1.27}$$

As in the case of the internal energy, the change in Helmholtz free energy may be related to the amount of work obtainable from the system. In a general infinitesimal process

$$\begin{aligned} dA &= dE - d(TS) \\ &= đQ - TdS - SdT - đW \ . \end{aligned} \tag{1.28}$$

Thus

$$đW = (đQ - TdS) - SdT - dA \ . \tag{1.29}$$

In a reversible transformation $đQ = TdS$. If the process is isothermal as well as reversible we have $đW = -dA$ and the Helmholtz free energy plays the role of a potential energy for reversible isothermal processes. If the process in question is isothermal but not reversible, we have $đQ - TdS \leq 0$ and

$$(đW)_{irrev} = đQ - TdS - dA \leq -dA \tag{1.30}$$

which shows that $-dA$ is the maximum amount of work that can be extracted, at constant temperature, from the system. We also see, from (1.30), that if the temperature and generalized displacements are fixed ($đW = 0$), a spontaneous process can only decrease the Helmholtz free energy and conclude that the equilibrium state of a system at fixed $(T, \{x_i\}, \{N_j\})$ is the state of minimum Helmholtz free energy.

Another thermodynamic potential which is often useful is the *Gibbs free energy* G. For a PVT system we write

$$G = A + PV \ . \tag{1.31}$$

This function is again a state function with a differential

$$dG = dA + PdV + VdP = -SdT + VdP = -SdT + VdP \ . \tag{1.32}$$

In a general process

$$dG = dE - d(TS) + d(PV) \tag{1.33}$$

$$= (đQ - TdS) - (đW - PdV) + VdP - SdT \ . \tag{1.34}$$

We see that the relations

$$\begin{aligned} đW - PdV &= 0 \\ đQ - TdS &\leq 0 \end{aligned} \tag{1.35}$$

imply that the Gibbs potential can only decrease in a spontaneous process at fixed T and P. It is also easy to show that the change in Gibbs potential is the maximum amount of work that can be extracted from a system through a process at fixed T and P. It follows that this occurs when the process is reversible.

In our microscopic statistical treatment of magnetic materials we will model these materials by systems of magnetic moments (or "spins") which can orient themselves in an applied magnetic field $\mathbf{H}$. The work done by the system, if the applied field is held constant, is then[2]

$$đW = -\mathbf{H} \cdot d\mathbf{M} \ . \tag{1.36}$$

Instead of defining yet another potential, we modify the definition of the Gibbs potential for a purely magnetic system to read

$$G(\mathbf{H}, T) = E(S, \mathbf{M}) - TS - \mathbf{M} \cdot \mathbf{H} \tag{1.37}$$

$$dG = -SdT - \mathbf{M} \cdot d\mathbf{H} \ . \tag{1.38}$$

It should be noted that (1.37) is not a universally accepted convention. Some authors refer to (1.37) as the Helmholtz free energy.

One further potential that is very useful in statistical physics is the grand potential $\Omega_G(T, V, \{\mu\})$. This potential is obtained from the internal energy through the transformation

$$\Omega_G(T, V, \{\mu\}) = E - TS - \sum_i N_i \mu_i \tag{1.39}$$

and has the differential

$$d\Omega_G = -SdT - PdV - \sum_i N_i d\mu_i \ . \tag{1.40}$$

The grand potential is necessary for the description of open systems or, equivalently, for systems that can exchange particles with their surroundings.

[2] For a discussion of work done by a magnet during a process in which its magnetization is changed, see Appendix B in Callen[48].