

For our purposes it is convenient to choose the grand potential  $\Omega$  as our preferred state function. It is the state function that describes the state of a system when the electrochemical potential, the volume and the temperature are chosen as independent variables. It is also the Legendre transform of the energy with respect to the temperature and the electrochemical potential:

$$\Omega \doteq E - TS - \mu N = -PU \quad (4.2)$$

Its definition is given by the equal-by-definition sign ( $\doteq$ ). The right-hand equality represents a property proven with generality [5].

Other thermodynamic variables that characterise the system in equilibrium can be obtained from the grand potential as derivatives. Hence, the number of particles, entropy and pressure of the system under consideration can be obtained as

$$N = - \left. \frac{\partial \Omega}{\partial \mu} \right|_{U,T}; \quad S = - \left. \frac{\partial \Omega}{\partial T} \right|_{U,\mu}; \quad P = - \left. \frac{\partial \Omega}{\partial U} \right|_{\mu,T} \quad (4.3)$$

For describing systems in non-equilibrium, the system under study is assumed to be subdivided into small subsystems each one comprising an elementary volume in the space-of-phases<sup>2</sup>  $(x, y, z, v_x, v_y, v_z)$  and having a size sufficient to allow the definition of thermodynamic magnitudes in it. Within such volumes, the subsystems are assumed to be in equilibrium. Thus, thermodynamic magnitudes are dependent on the position  $\mathbf{r} \doteq (x, y, z)$  of the elementary volume and the velocity of motion  $\mathbf{v} \doteq (v_x, v_y, v_z)$  of the elementary bodies or particles in it.

For describing the system in non-equilibrium, it is necessary to introduce the concept of *thermodynamic current densities* [6],  $\mathbf{j}_x$ . They are related to the extensive variables  $X$  and are defined for those elementary bodies with velocity  $\mathbf{v}$  at the point  $\mathbf{r}$  as follows:

$$\mathbf{j}_x(\mathbf{r}, \mathbf{v}) = x(\mathbf{r}, \mathbf{v}) \mathbf{v} \quad (4.4)$$

where  $x = X/U$  is the contribution to the extensive variable  $X$ , per unit of volume  $U$  at the point  $\mathbf{r}$  of the elementary bodies with velocity  $\mathbf{v}$ .

Equation (4.2) can be applied to the thermodynamic current densities allowing us to write

$$\mathbf{j}_\omega = \mathbf{j}_e - T(\mathbf{r}, \mathbf{v})\mathbf{j}_s - \mu(\mathbf{r}, \mathbf{v})\mathbf{j}_n = -P(\mathbf{r}, \mathbf{v}) \mathbf{v} \quad (4.5)$$

For the thermodynamic current densities, we can write the following continuity equations [7]:

$$g \doteq \frac{\partial n}{\partial t} + \nabla \cdot \mathbf{j}_n \quad (4.6)$$

$$\nu \doteq \frac{\partial e}{\partial t} + \nabla \cdot \mathbf{j}_e \quad (4.7)$$

$$\sigma \doteq \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{j}_s \quad (4.8)$$

<sup>2</sup>  $x, y$  and  $z$  are the spatial co-ordinates giving the position of the particle and  $v_x, v_y$  and  $v_z$  are the co-ordinates of its velocity.