for $\Delta\dot{w} \geq 0$, is obtained for $T_r = T_s$, although unfortunately it occurs when $\Delta\dot{w} = 0$, that is, when negligible (actually, none) work is done by the cell. However, this is a general characteristic of reversible engines, which yield the Carnot efficiency only at the expense of producing negligible power.

4.3.3 Thermodynamic Consistence of the Shockley–Queisser Photovoltaic Cell

Electrons and photons are the main particles interacting in a solar cell [8]. However, other interactions occur as well. In general, looking at equation (4.13), the generation of entropy for each kind of particle (electrons, photons and others) is written as

$$\sigma = \sum_i \left[\frac{1}{T}\upsilon + \boldsymbol{j}_e \nabla \frac{1}{T} - \frac{\mu}{T} g - \boldsymbol{j}_n \nabla \frac{\mu}{T} + \nabla \cdot \left(-\frac{1}{T} \boldsymbol{j}_\omega \right) \right] \tag{4.28}$$

where the summation extends to the different states of the particle.

First we analyse the generation of entropy by electrons, σ_{ele}. Except for the case of ballistic electrons, the pressure – appearing inside $\boldsymbol{j}_\omega$ as shown in equation (4.5) – is very quickly equilibrated; it is the same for $+\boldsymbol{v}$ and for $-\boldsymbol{v}$ as a result of the frequent elastic collisions. Thus, the term in $\boldsymbol{j}_\omega$ for electrons disappears when the sum is extended to all the states in each energy. These collisions also cause the temperature and the free energy to become the same for all the directions, at least for a given energy. Furthermore, in conventional solar cells, the temperature of the electrons is the same for any energy and is equal to the lattice temperature T_a. Also, the electrochemical potential is the same for all the electrons within the same band at a given $\boldsymbol{r}$.

In a real cell, the energy flow $\boldsymbol{j}_e$ goes from the high-temperature regions towards the low-temperature ones $[\nabla(1/T) \geq 0]$ so that the term in (4.28) involving $\boldsymbol{j}_e$ produces positive entropy. The electron flow, $\boldsymbol{j}_n$, opposes the gradient of electrochemical potential, thus also producing positive entropy for constant temperature. However, in the ideal cell, the lattice temperature, which is also that of the electrons, is constant and the term involving $\nabla(1/T)$ disappears. Furthermore, in the SQ [2] ideal cell, mobility is infinite and, therefore, its conduction and valence band electrochemical potentials or quasi-Fermi levels $(\varepsilon_{Fc}, \varepsilon_{Fv})$ are constant throughout the whole solar cell and their gradients are also zero. Therefore, all the gradients in equation (4.28) disappear and the electron contribution to entropy generation, σ_{ele}, is given by

$$\sigma_{\text{ele}} = \sum_{i-\text{ele}} \left[\frac{1}{T_a} \upsilon_{i-\text{ele}} - \frac{\varepsilon_{Fc(v)}}{T_a} g_{i-\text{ele}} \right] \tag{4.29}$$

The quasi-Fermi level to be used in this case is ε_{Fc} or ε_{Fv} depending on the band to which the electronic state i-ele belongs. This is represented by $\varepsilon_{Fc(v)}$.

Other interactions may occur in the cell involving other particles besides the electrons and the photons. We shall assume that in these interactions the bodies involved (labelled as *others*) also have a direction-independent pressure and that they are also at