

the lattice temperature. Furthermore, if these particles exist, they are assumed to have zero chemical potential (as it is the case, for example, of the phonons). Using these assumptions, the contribution to the irreversible entropy generation rate from these *other* particles becomes

$$\sigma_{\text{others}} = \sum_{i-\text{others}} \left[\frac{1}{T_a} v_{i-\text{others}} \right] \quad (4.30)$$

For the case of the photons, the situation is rather different. As said before, photons do not interact with each other and, therefore, they are essentially ballistic. Their thermodynamic intensive variables may experience variations with the photon energy and also with their direction of propagation. In fact, they come from the sun in a few directions only, and only in these directions do they exert a pressure. The direct consequence is that a non-vanishing current of grand potential exists for the photons. (It vanishes in gases of photons that are confined and in thermal equilibrium with the confining walls. Using this condition for photon beams from the sun is not correct.)

N_{ph} being the number of photons in a mode corresponding to a certain ray moving inside the semiconductor, their evolution along a given ray path corresponding to a radiation mode is given by [17]

$$N_{\text{ph}}(\zeta) = f_{\text{BE}}(T, qV)[1 - e^{-\alpha\zeta}] + N_{\text{ph}}(0)e^{-\alpha\zeta} \quad (4.31)$$

where ζ is the length of the ray, f_{BE} is the Bose–Einstein factor for luminescent photons whose chemical potential is the separation between the conduction and the valence band electron quasi-Fermi levels – in this case equalling the cell voltage V (times q) – and α is the absorption coefficient. Equation (4.31) shows a non-homogeneous profile for N_{ph} contributed to by luminescent photons that increase with ζ (first term on the right-hand side) and externally fed photons that decrease when the ray proceeds across the semiconductor (second term), and these photons are absorbed. $N_{\text{ph}}(0) = f_{\text{BE}}(T_s, 0)$ is usually taken in solar cells that correspond to illumination by free (i.e. with zero chemical potential) radiation at the sun temperature T_s .

In general, the photons in a mode of energy ε are considered as a macroscopic body [9] for which temperature and chemical potential can be defined. However, thermodynamically, they can be arbitrarily characterised by a chemical potential μ and a temperature T as long as $(\varepsilon - \mu)/T$ takes the same value. For example, the incident solar photons may be considered at the solar temperature T_s with zero chemical potential or, alternatively, at room temperature T_a with an energy variable chemical potential $\mu_s = \varepsilon(1 - T_a/T_s)$. This property has already been used in the study of the monochromatic cell.

Indeed, this arbitrary choice of T and μ does not affect the entropy production. This becomes evident if we rewrite equation (4.28) in the case of photons as

$$\sigma_{\text{ph}} = \sum_{i-\text{ph}} \left[\frac{\varepsilon - \mu}{T} g + \mathbf{j}_n \cdot \nabla \left(\frac{\varepsilon - \mu}{T} \right) + \nabla \cdot \left(-\frac{1}{T} \mathbf{j}_\omega \right) \right] \quad (4.32)$$

where we have made use of equation (4.15) and of the fact that $v = \varepsilon g$. This equation depends explicitly only on $(\varepsilon - \mu)/T$. This is less evident in the term in \mathbf{j}_ω/T , but as