

$\mathbf{j}_e \nabla 1/T$ ), free energy ( $\mu g$ ) generation, Joule effect ( $\mathbf{j}_n \nabla \mu$ ) and expansion of the volume that contains the particles ( $\nabla \mathbf{j}_\omega/T$ ). This equation is very important and will be used to prove the thermodynamic consistence of solar cells.

#### 4.2.4 An Integral View

Fluxes,  $\dot{X}$ , of the thermodynamic currents,  $\mathbf{j}_x$ , will be frequently used in this paper. In this text, they will be also called *thermodynamic variable rates*. By definition, the following relationship exists:

$$\dot{X} \doteq \int_A \sum_i \mathbf{j}_x \, dA \quad (4.14)$$

where the sum refers to the different subsystems with different velocities to be found at a given position.  $A$  is the surface through which the flux is calculated. Actually,  $\mathbf{j}_x \, dA$  represents the scalar product of the current density vector  $\mathbf{j}_x$  and the oriented surface element  $dA$  (orientation is arbitrary and if a relevant volume exists the orientation selected leads to the definition of *escaping* or *entering* rates).

#### 4.2.5 Thermodynamic Functions of Radiation

The number of photons in a given mode of radiation is given [9] by the well-known Bose–Einstein factor  $f_{\text{BE}} = \{\exp[(\varepsilon - \mu)/kT] - 1\}^{-1}$ , which through equation (4.3) is related to the grand canonical potential  $\Omega = kT \ln\{\exp[(\mu - \varepsilon)/kT] - 1\}$ . In these equations, most of the symbols have been defined earlier:  $\varepsilon$  is the photon energy in the mode and  $k$  is the Boltzman constant. The corresponding thermodynamic current densities for these photons are

$$\mathbf{j}_n = f_{\text{BE}} \mathbf{c}/(Un_r); \quad \mathbf{j}_e = \varepsilon \mathbf{j}_n f_{\text{BE}} \mathbf{c}/(Un_r); \quad \mathbf{j}_\omega = \Omega \mathbf{c}/(Un_r) \quad (4.15)$$

where  $\mathbf{c}$  is the light velocity (a vector since it includes its direction) in the vacuum and  $n_r$  is the index of refraction of the medium in which the photons propagate, which is assumed to be independent of the direction of propagation. Thus,  $\mathbf{c}/n_r$  is the velocity of the photons in the medium.

The number of photon modes with energy between  $\varepsilon$  and  $\varepsilon + d\varepsilon$  is  $8\pi Un_r^3 \varepsilon^2 / (h^3 \mathbf{c}^2) d\varepsilon$ . When the modes with energies  $\varepsilon_m < \varepsilon < \varepsilon_M$  are taken into account, the total grand canonical potential of the photons,  $\Omega_{\text{ph}}$ , associated with these modes is the sum of the contributions from each mode and can be written as

$$\Omega_{\text{ph}}(U, T, \mu) = \frac{8\pi Un_r^3}{h^3 \mathbf{c}^3} \int_{\varepsilon_m}^{\varepsilon_M} \varepsilon^2 kT \ln(1 - e^{(\mu - \varepsilon)/kT}) d\varepsilon \quad (4.16)$$

where  $h$  is the Planck's constant.

Photons do not interact among themselves, such that temperatures and chemical potentials can be different for each mode. This means that they can be a function of the energy and of the direction of propagation. In the non-equilibrium case they can also be a