CHAPTER II

THE GENERALIZED DIFFUSIVITY-MOBILITY RATIO

The diffusivity-mobility ratio or the relation between the diffusion coefficient D and mobility μ of the carriers with charge q of a semiconductor at finite temperature T in simple case or completely non-degenerate case is found to be[5]

$$\frac{D}{\mu} = \frac{k_B T}{|q|}. \tag{2.1}$$

This relation is found by Einstein in the context of Brownian motion.

For the generalized diffusivity-mobility ratio, Landsberg[6] applied a concept of diffusion of charged particles in a semiconductor in 1952, as we show later. In this chapter we shall denote the electrochemical potential for charged particles by λ. However, it is convenient to introduce also the chemical potential λ_0 of a component in a system. It will be recalled from thermodynamics that λ_0 plays the same role as regards equilibrium with respect to particle diffusion or chemical equilibrium, as temperature, T, does with respect to heat conduction or thermal equilibrium. That T, λ_0 and also pressure P are on the same footing may be seen from the Gibb's equation for the mean energy U of a system of N neutral particles, which is

$$dU = TdS - PdV + \lambda_0 dN, \tag{2.2}$$

where S, V are entropy and volume, respectively. For a system of particles of charge q (positive or negative) a change in the number of particles lead to additional energy term $q\varphi\, dN$, where $\varphi(\vec{r})$ is the electrostatic potential at position $\vec{r}$ being considered.

Hence, the analogue of (2.2) for a system of charged particles is

$$dU = TdS - PdV + (\lambda_0 + q\varphi)dN. \tag{2.3}$$

Many thermodynamic functions need to be amended by virtue of this change, and λ_0 has to be replaced by the electrochemical potential

$$\lambda = \lambda_0 + q\varphi. \tag{2.4}$$

In semiconductor work, we deal with electronic states in the conduction band and vacancies in electronic states in valence bands. At equilibrium, they can be treated in terms of a single electrochemical potential λ. This chemical potential pertains to electronic states so that q is negative. Consequently the change of λ with φ is given by

$$\lambda = \lambda_0 - |q|\varphi. \tag{2.5}$$

Suppose now that λ_0 depends on the position $\vec{r}$ through the $\vec{r}$-dependence of a general carrier concentration n and the temperature T. We then have, using (2.5), that the electric field is given by

$$\vec{E} = -\nabla\varphi$$

$$= \frac{1}{|q|}\nabla(\lambda - \lambda_0)$$

$$= \frac{1}{|q|}\left\{\nabla\lambda - \left(\frac{\partial\lambda_0}{\partial n}\right)_{T,V}\nabla n - \left(\frac{\partial\lambda_0}{\partial T}\right)_{n,V}\nabla T\right\}. \qquad (2.6)$$

Now, the current density $\vec{j}$ due to the current carriers of concentration n is the sum of a conduction current density $|q|\mu n\vec{E}$ and a diffusion current density of $-qD\nabla n$. For uniform temperature,

$$\vec{j} = |q|\mu n\vec{E} - qD\nabla n$$

$$= \mu n\left[\nabla\lambda - \frac{\partial\lambda_0}{\partial n}\nabla n\right] - qD\nabla n. \qquad (2.7)$$

We also note that from irreversible thermodynamics

$$\vec{j} = \mu n\nabla\lambda. \qquad (2.8)$$

so that the coefficient of ∇n in (2.7) must vanish. One needs not appeal to (2.8) if one observes that in thermal equilibrium $\nabla \lambda = 0$ from thermodynamics, that $\vec{j} = 0$ by hypothesis, so that the coefficient of ∇n in (2.7) must vanish. The relation obtained may then be expected to be valid also away from but in the neighborhood of equilibrium. Hence

$$\frac{|q|}{n}\frac{D}{\mu} = -\frac{|q|}{q}\left(\frac{\partial \lambda_0}{\partial n}\right)_{T,V}. \qquad (2.9)$$

Since λ and λ_0 differ by a quantity ($|q|\varphi$) which can normally be regarded as independence of n, one finally finds

$$\frac{D}{\mu} = -\frac{n}{q}\left(\frac{\partial \lambda}{\partial n}\right)_{T,V}, \qquad (2.10)$$

this is the generalized diffusivity-mobility ratio. In the semiconductor work , the electrochemical potential λ is the same as the Fermi energy E_f and in our work we deal with n-type semiconductors, majority carriers are electrons with charge e, so (2.10) can be rewritten as

$$\frac{D}{\mu} = \frac{n}{e}\left(\frac{\partial E_f}{\partial n}\right)_{T,V}, \qquad (2.11)$$

equation (2.11) is an important relation which is used to derive the diffusivity-mobility ratio for n-type heavily doped semiconductors in Chapter IV, and to derive by Van Cong and Debiais an empirical diffusivity-mobility ratio.

Note that for Maxwell-Boltzmann distribution of electrons or holes of concentration n and p, respectively, and with A_e, A_h the appropriate functions of temperature and volume

$$n \rightarrow \begin{cases} n = A_e \exp\left(\lambda/k_B T\right) \\ p = A_h \exp\left(-\lambda/k_B T\right) \end{cases}, \tag{2.12}$$

so that one has

$$\frac{D}{\mu} = \frac{k_B T}{|q|},$$

as the diffusivity-mobility ratio in completely non-degenerate case as (2.1).