13.10 The Einstein-Nernst relation

If a particle of mass m carries an electric charge q and is exposed to an electric field $\boldsymbol{E}$, then in addition to viscosity $-\boldsymbol{v}/B$ and random buffeting $\boldsymbol{f}$, the constant force $q\boldsymbol{E}$ acts on it

$$m\,\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{B} + q\boldsymbol{E} + \boldsymbol{f}. \tag{13.138}$$

The mean value of its velocity will then satisfy the differential equation

$$\left\langle \frac{d\boldsymbol{v}}{dt} \right\rangle = -\frac{\langle \boldsymbol{v} \rangle}{\tau} + \frac{q\boldsymbol{E}}{m} \tag{13.139}$$

where $\tau = mB$. A particular solution of this inhomogeneous equation is

$$\langle \boldsymbol{v}(t) \rangle_{pi} = \frac{q\tau\boldsymbol{E}}{m} = qB\boldsymbol{E}. \tag{13.140}$$

The general solution of its homogeneous version is $\langle \boldsymbol{v}(t) \rangle_{gh} = \boldsymbol{A}\exp(-t/\tau)$ in which the constant $\boldsymbol{A}$ is chosen to give $\langle \boldsymbol{v}(0) \rangle$ at $t = 0$. So by (6.13), the general solution $\langle \boldsymbol{v}(t) \rangle$ to equation (13.139) is (exercise 13.19) the sum of $\langle \boldsymbol{v}(t) \rangle_{pi}$ and $\langle \boldsymbol{v}(t) \rangle_{gh}$

$$\langle \boldsymbol{v}(t) \rangle = qB\boldsymbol{E} + \left[\langle \boldsymbol{v}(0) \rangle - qB\boldsymbol{E} \right] e^{-t/\tau}. \tag{13.141}$$

By applying the tricks of the previous section (13.9), one may show (exercise 13.20) that the variance of the position $\boldsymbol{r}$ about its mean $\langle \boldsymbol{r}(t) \rangle$ is

$$\left\langle (\boldsymbol{r} - \langle \boldsymbol{r}(t) \rangle)^2 \right\rangle = \frac{6kT\tau^2}{m} \left(\frac{t}{\tau} - 1 + e^{-t/\tau} \right) \tag{13.142}$$

where $\langle \boldsymbol{r}(t) \rangle = (q\tau^2\boldsymbol{E}/m)\left(t/\tau - 1 + e^{-t/\tau}\right)$ if $\langle \boldsymbol{r}(0) \rangle = \langle \boldsymbol{v}(0) \rangle = 0$. So for times $t \gg \tau$, this variance is

$$\left\langle (\boldsymbol{r} - \langle \boldsymbol{r}(t) \rangle)^2 \right\rangle = \frac{6kT\tau t}{m}. \tag{13.143}$$

Since the diffusion constant D is defined by (13.134) as

$$\left\langle (\boldsymbol{r} - \langle \boldsymbol{r}(t) \rangle)^2 \right\rangle = 6\,D\,t \tag{13.144}$$

we arrive at the Einstein-Nernst relation

$$D = BkT = \frac{qB}{q}kT = \frac{\mu}{q}kT \tag{13.145}$$

in which the electric mobility is $\mu = qB$.