11.B.4. Self-Diffusion

In general, diffusion is the process of equalizing the spatially varying concentration of particles.

In an ordinary diffusion, varying concentration is also accompanied by the variation of at least one mechanical property. For example, diffusion caused by a density gradient is accompanied by a varying mechanical property, mass.

In an ideal self-diffusion, differences in the concentration of particles are not accompanied by any variations in mechanical properties. The phenomenon is therefore a purely statistical effect, as is the theoretical definition of diffusion.

In practice, one way to approximate self-diffusion is to inject, into a localized region, a small (trace) amount of radioactive particles isotopic to those in an otherwise homogeneous system. By monitoring the concentration of these tracer particles, one can determine the coefficient of self-diffusion D.

We now turn to derive an expression for D.

Without loss of generality, we consider the quasi-1-D problem of diffusion across the x-y plane at $z = 0$.

Let

$n = \text{const} =$ total density of particles.

$n_T(\boldsymbol{r}) =$ density of tracer particles.

$dS =$ surface element, centered at the origin, of the x-y plane

$dV_+ =$ volume element centered at point $\boldsymbol{r} = (r, \theta, \phi)$ above the x-y plane.

$f =$ collision frequency between particles (tracer or normal).

$d\dot{N}_+ =$ average number of tracer particles hitting dS from dV_+ per unit time.

For the diffusion process, $d\dot{N}_+$ counts only tracer particles that are first randomized by a collision inside dV_+, then travel and reach dS without collision.

Using

$$f\, n_T\, dV = \frac{\langle v \rangle}{\lambda}\, n_T\, dV \qquad \text{[(11.17) used.]}$$

= average number of tracer particles undergoing collisions in dV per unit time.

$d\Omega \approx \frac{|\cos\theta|}{r^2}\, dS =$ solid angle subtended by dS at dV (or $\boldsymbol{r}$) for $r \gg \sqrt{dS}$.

$\frac{d\Omega}{4\pi} =$ fraction of particles in dV aimed at dS, assuming random motion.

$e^{-r/\lambda} =$ probability of a particle travelling from dV to dS without suffering any collision.

we have

$$d\dot{N}_+ = \left(\frac{\langle v \rangle}{\lambda}\, n_T(\boldsymbol{r})\, dV_+ \right) \left(\frac{|\cos\theta|}{4\pi r^2}\, dS \right) e^{-r/\lambda}$$

(11.18)

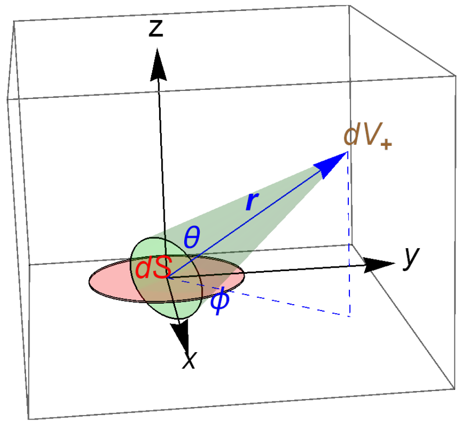

Fig. 11.2. Solid angle $d\Omega'$ (apex angle of green cone) subtended by $\cos\theta\, dS$ at dV_+ (or $\boldsymbol{r}$).

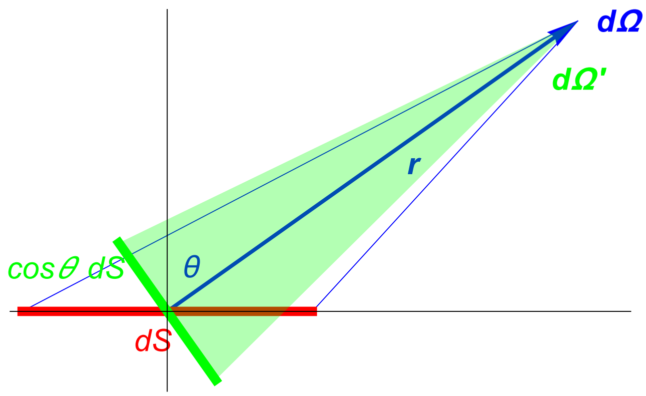

Fig. 11.2a. Solid angle $d\Omega$ subtended by dS at $\boldsymbol{r}$ and solid angle $d\Omega'$ subtended by $\cos\theta\, dS$ at $\boldsymbol{r}$.

For $r \gg \sqrt{dS}$, $d\Omega' \approx d\Omega$.

The (diffusion) flux $J^D_{z+}(\boldsymbol{r})$ of tracer particles going through the x-y plane at $\boldsymbol{r} = 0$ from above is therefore

$$J^D_{z+}(\mathbf{0}) = \frac{1}{dS}\int_{z\geq 0} d\dot{N}_+$$
$$= \frac{\langle v\rangle}{4\pi\lambda}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin\theta \int_0^{\infty} dr\, r^2\, n_T(\boldsymbol{r})\,\frac{\cos\theta}{r^2}\, e^{-r/\lambda}$$

(11.19)

For $n_T(\boldsymbol{r}) = \text{const}$, (11.19) reduces to

$$J^D_{z+}(\mathbf{0}) = \frac{\langle v\rangle n_T}{4\pi\lambda}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta\, \sin\theta \int_0^{\infty} dr\, \cos\theta\, e^{-r/\lambda}$$
$$= \frac{\langle v\rangle n_T}{4\pi\lambda}\, 2\pi\left(\frac{1}{2}\cos^2\theta\right)_0^{\pi/2}\left(-\lambda\, e^{-r/\lambda}\right)_0^{\infty}$$
$$= -\frac{1}{4}\langle v\rangle n_T$$

(11.19a)

Similarly, the flux $J^D_{z-}(\mathbf{0})$ of tracer particles going through the x-y plane at $\boldsymbol{r} = \mathbf{0}$ from below is

$$J^D_{z-}(\mathbf{0}) = \frac{1}{dS}\int_{z\leq 0} d\dot{N}_-$$

$$= \frac{\langle v \rangle}{4\pi\lambda} \int_0^{2\pi} d\phi \int_{\pi/2}^{\pi} d\theta \sin\theta \int_0^{\infty} dr\, r^2\, n_T(\boldsymbol{r}) \frac{-\cos\theta}{r^2} e^{-r/\lambda} \quad (11.19b)$$

The net flux $J_z(\mathbf{0})$ of tracer particles passing through the x-y plane at $\boldsymbol{r} = \mathbf{0}$ (towards the $+z$ direction) is therefore

$$J_z^D(\mathbf{0}) = J_{z-}^D(\mathbf{0}) - J_{z+}^D(\mathbf{0})$$
$$= -\frac{\langle v \rangle}{4\pi\lambda} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr\, n_T(\boldsymbol{r}) \cos\theta\, e^{-r/\lambda} \quad (11.21)$$

Owing to the rapidly decaying factor $e^{-r/\lambda}$, we need keep only a few terms in the Taylor expansion

$$n_T(\boldsymbol{r}) = n_T(\mathbf{0}) + \boldsymbol{r}\cdot\nabla n_T(\mathbf{0}) + \frac{1}{2}(\boldsymbol{r}\cdot\nabla)^2 n_T(\mathbf{0}) + \ldots \quad (11.20)$$

where

$$\boldsymbol{r}\cdot\nabla = r\left(\sin\theta\cos\phi \frac{\partial}{\partial x} + \sin\theta\sin\phi \frac{\partial}{\partial y} + \cos\theta \frac{\partial}{\partial z}\right) \quad (11.20a)$$

Since the ϕ integrals all vanish, we have, to the lowest order of r,

$$J_z^D(\mathbf{0}) \approx -\frac{\langle v \rangle}{4\pi\lambda} \int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\theta \int_0^{\infty} dr\, r \left(\frac{\partial n_T}{\partial z}\right)_0 \cos^2\theta\, e^{-r/\lambda}$$
$$= -\frac{\langle v \rangle}{4\pi\lambda} (2\pi) \left(\frac{2}{3}\right) \left(\frac{\partial n_T}{\partial z}\right)_0 \lambda^2$$
$$= -\frac{\langle v \rangle \lambda}{3} \left(\frac{\partial n_T}{\partial z}\right)_0 \quad (11.22)$$

By adjusting the coordinate origin and orientation, we can generalize (11.22) to

$$\boldsymbol{J}^D(\boldsymbol{r}) = -\frac{\langle v \rangle \lambda}{3} \nabla_{\boldsymbol{r}} n_T(\boldsymbol{r})$$
$$= -D\, \nabla_{\boldsymbol{r}} n_T(\boldsymbol{r})$$

(11.25)

where

$$D = \frac{\langle v \rangle \lambda}{3}$$

(11.24)

is the coefficient of self-diffusion and (11.25) is known as the Fick’s law.

Since the number of tracer particles is conserved, the balance equation for n_T is [c.f. (10.3) of §10.B.1.1]

$$\frac{\partial n_T}{\partial t} + \nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}^D = 0$$

Using (11.25), we recover the familiar diffusion equation

$$\frac{\partial n_T}{\partial t} = D\, \nabla_{\boldsymbol{r}}^2 n_T \quad (11.28)$$

which was previously derived using random walk [see §5.C.2].