

12.8.2: The Diffusion Constant

The diffusive flow of particles can be studied by applying a constant force f to a system using the microscopic equations of motion

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i(\mathbf{q}_1, \dots, \mathbf{q}_N) + f\hat{\mathbf{x}}$$

which have the conserved energy

$$H' = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{q}_1, \dots, \mathbf{q}_N) - f \sum_{i=1}^N x_i$$

Since the force is applied in the $\hat{\mathbf{x}}$ direction, there will be a net flow of particles in this direction, i.e., a current J_x . Since this current is a thermodynamic quantity, there is an estimator for it:

$$u_x = \sum_{i=1}^N \dot{x}_i$$

and $J_x = \langle u_x \rangle$. The constant force can be considered as arising from a potential field

$$\phi(x) = -xf$$

The potential gradient $\partial\phi/\partial x$ will give rise to a concentration gradient $\partial c/\partial x$ which is opposite to the potential gradient and related to it by

$$\frac{\partial c}{\partial x} = -\frac{1}{kT} \frac{\partial \phi}{\partial x}$$

However, [Fick's law](#) tells how to relate the particle current J_x to the concentration gradient

$$\begin{aligned} J_x &= D \frac{\partial c}{\partial x} \\ &= -\frac{D}{kT} \frac{\partial \phi}{\partial x} \\ &= \frac{D}{kT} f \end{aligned}$$

where D is the **diffusion constant**. Solving for D gives

$$\begin{aligned} D &= kT \frac{J_x}{f} \\ &= kT \lim_{t \rightarrow \infty} \frac{\langle u_x(t) \rangle}{f} \end{aligned}$$

Let us apply the linear response formula again to the above nonequilibrium average. Again, we make the identification:

$$F_e(t) = 1 \quad \mathbf{D}_i = f\hat{\mathbf{x}} \quad \mathbf{C}_i = 0$$

Thus,

$$\begin{aligned} \langle u_x(t) \rangle &= \langle u_x \rangle_0 + \beta \int_0^t ds f \left\langle \left(\sum_{i=1}^N \dot{x}_i(0) \right) \left(\sum_{i=1}^N \dot{x}_i(t-s) \right) \right\rangle_0 \\ &= \langle u_x \rangle_0 + \beta f \int_0^t ds \sum_{i,j} \langle \dot{x}_i(0) \dot{x}_j(t-s) \rangle_0 \end{aligned}$$

In equilibrium, it can be shown that there are no cross correlations between different particles. Consider the initial value of the correlation function. From the virial theorem, we have

$$\langle \dot{x}_i \dot{x}_j \rangle_0 = \delta_{ij} \langle \dot{x}_i^2 \rangle_0$$

which vanishes for $i \neq j$. In general,

$$\langle \dot{x}_i(0) \dot{x}_j(t) \rangle_0 = \delta_{ij} \langle \dot{x}_i(0) \dot{x}_i(t-s) \rangle_0$$

Thus,

$$\langle u_x(t) \rangle = \langle u_x \rangle_0 + \beta f \int_0^t ds \sum_{i=1}^N \dot{x}_i(0) \dot{x}_i(t-s) \rangle_0$$

In equilibrium, $\langle u_x \rangle_0 = 0$ being linear in the velocities (hence momenta). Thus, the diffusion constant is given by, when the limit $t \rightarrow \infty$ is taken,

$$D = \int_0^\infty \sum_{i=1}^N \langle \dot{x}_i(0) \dot{x}_i(t) \rangle_0$$

However, since no spatial direction is preferred, we could also choose to apply the external force in the y or z directions and average the result over these three. This would give a diffusion constant

$$D = \frac{1}{3} \int_0^\infty dt \sum_{i=1}^N \langle \dot{\mathbf{r}}_i(0) \cdot \dot{\mathbf{r}}_i(t) \rangle_0$$

The quantity

$$\sum_{i=1}^N \langle \dot{\mathbf{r}}_i(0) \cdot \dot{\mathbf{r}}_i(t) \rangle_0$$

is known as the **velocity autocorrelation function**, a quantity we will encounter again in other contexts.

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