

# Chapter 2

## Theory

In this chapter I will give the fundamental concepts to describe diffusion on the atomic level, with special consideration to the case of diffusion on a lattice. For reasons of conceptual simplicity this chapter will stay abstract, I will work out the connection to the actual problem at hand—atomic diffusion in condensed matter—in [Chap. 3](#).

### 2.1 Setting the Scene

The system to be described consists of particles diffusing in infinite space. The particles behave equally but are distinguishable. The theoretical tools for the problem at hand, i.e. to describe the stochastic motion of the particles, were given by van Hove [12]. These are:

- The *self-correlation function*  $G_s(\Delta\vec{x}, \Delta t)$  gives the probability to find a *given* particle at time  $t + \Delta t$  at the position  $\vec{x} + \Delta\vec{x}$  given that it (the *same* particle) was at time  $t$  at position  $\vec{x}$ .
- The *pair-correlation function*  $G(\Delta\vec{x}, \Delta t)$  gives the probability to find *any* particle at time  $t + \Delta t$  at the position  $\vec{x} + \Delta\vec{x}$  given that *any* particle was at time  $t$  at position  $\vec{x}$ .

The definition given above is the classical case of van Hove's quantum-mechanical theory. This is justified by the fact that first for the systems of interest in this thesis the spatial uncertainty of the particles is given by thermal excitations and not quantum effects (e.g. tunneling) and second that the scattering of X-rays on diffusing atoms can be considered truly elastic due to the X-rays' high energy. The formulation with time differences instead of the correlations between two absolute times implies that the system is in equilibrium. Obviously the functions given above do not contain all the information of the dynamic process. One could continue and consider correlation functions of higher order, e.g. the probability of a particle being at a given time and place if it was at time  $t_1$  at place  $\vec{x}_1$  and at time  $t_2$  at place  $\vec{x}_2$ , but for diffusion modelled as a Markov process the description by two-point correlations suffices.

From now on I will restrict my attention to particles diffusing on a lattice. I assume the lattice to be three-dimensional, as this covers all cases treated later in this thesis, but this is just for convenience, the reader is invited to picture a lattice of arbitrary finite dimensionality,<sup>1</sup> everything given here generalizes. Let the lattice be composed of  $\Lambda$  sublattices. The translation vectors of the fundamental lattice be  $\vec{a}_1$ ,  $\vec{a}_2$ , and  $\vec{a}_3$ , being linearly independent, but not necessarily orthogonal. I use this basis set for spanning  $\mathbb{R}^3$ . The distinct sites in the sublattice have the coordinate vectors  $\mathbf{r}_\lambda$  for  $1 \leq \lambda \leq \Lambda$ . Finally I define the vectors spanning reciprocal space  $\vec{b}_1$ ,  $\vec{b}_2$ , and  $\vec{b}_3$  such that  $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{i,j}$ . This set of vectors can easily be constructed:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad (2.1.1)$$

$\vec{b}_2$  and  $\vec{b}_3$  follow by cyclic permutation. Given a vector  $\vec{x}$  relative to the Cartesian unity vectors  $\vec{e}_i$  I will write  $\mathbf{x}$  for its coordinate vector relative to the translation vectors of the lattice  $\vec{a}_i$ , analogously with a reciprocal vector  $\vec{q}$  and its coordinate vector  $\mathbf{q}$  relative to the reciprocal lattice vectors  $\vec{b}_i$ . This has the property that the valid positions of the particles are given by  $\mathbf{x} + \mathbf{r}_\lambda$  for  $\mathbf{x} \in \mathbb{Z}^3$  and  $1 \leq \lambda \leq \Lambda$ . Also note that  $\mathbf{q} \cdot \mathbf{x} = \vec{q} \cdot \vec{x}$  due to the definition of the reciprocal lattice vectors.

Having this definitions out of the way, I now move on to the description of the dynamics, the correlation functions.

## 2.2 The Self-Correlation Function

As stated above, van Hove's self-correlation function  $G_s(\Delta\mathbf{x}, \Delta t)$  gives the conditional probability for a given particle to be at time  $t + \Delta t$  at position  $\mathbf{x} + \Delta\mathbf{x}$  under the condition that this particle was at time  $t$  at position  $\mathbf{x}$ . The reason for treating the self-correlation function is first that it is a rather intuitive way of describing dynamics and second that there are methods which (more or less) directly measure it (see Sect. 3.4). These methods realize the measurement of the probability via the actual displacements of a vast number of atoms. I will now deduce the temporal evolution of this probability density. For past approaches to this problem see [2, 6, 7, 9, 10].

I consider particles diffusing on a lattice. As its name already tells, for the self-correlation function the movement of a particle with respect to itself alone is of relevance. Therefore it suffices to consider (the probability distribution of) the positions of one particle over time. In reality particles can interact, so actually the temporal evolution of the tagged particle's position is influenced by the configuration of its surrounding. As I describe the state of the system only by the position of the one

---

<sup>1</sup> Diffusion on a surface would be a physically relevant case of diffusion on a lower-dimensional lattice.

tagged particle, this fact can lead to a non-Markovian behaviour of the system (earlier states of the system can influence the hidden variables, i.e. the configuration of the neighbourhood, influencing in turn the further evolution). The simplification which makes the problem tractable is to postulate Markovian behaviour, i.e. that the probability distribution of the states of the system at some later time are only a function of the state of the system now.

The temporal evolution of the probability density is therefore defined by specifying the transition rates between the sites on the lattice. I write  $(\mathbf{K}(\Delta\mathbf{x}))_{\mu,\lambda}$  for the transition rate of the particle from sublattice  $\lambda$  in the cell  $\mathbf{x}$  to sublattice  $\mu$  in the cell  $\mathbf{x} + \Delta\mathbf{x}$ . Put another way, the entry in row  $\mu$ , column  $\lambda$  of the matrix  $\mathbf{K}(\Delta\mathbf{x})$  multiplied by an infinitesimal amount of time is the probability for a particle on the sublattice  $\lambda$  to jump onto the site  $\mu$  of the cell displaced by  $\Delta\mathbf{x}$  within this amount of time. For mass conservation I put the overall leaving rate from the sublattice  $\lambda$  into  $(\mathbf{K}(\mathbf{o}))_{\lambda,\lambda}$  but counted negatively:

$$\sum_{(\Delta\mathbf{x}, \mu) \neq (0, \lambda)} (\mathbf{K}(\Delta\mathbf{x}))_{\mu,\lambda} = -(\mathbf{K}(\mathbf{o}))_{\lambda,\lambda}. \quad (2.2.1)$$

I require detailed balance, this means that in equilibrium there should be no net flux between two states of the system:

$$(\mathbf{K}(\Delta\mathbf{x}))_{\mu,\lambda} p_\lambda = (\mathbf{K}(-\Delta\mathbf{x}))_{\lambda,\mu} p_\mu \quad (2.2.2)$$

where  $p_\lambda$  is the equilibrium probability for a particle to reside on sublattice  $\lambda$ .

My goal is to compute the temporal evolution of probabilities, so I introduce an ensemble of systems (i.e. an ensemble of particles). This ensemble is completely specified by  $(c(\mathbf{x}, t))_\lambda$ , the concentration (i.e. the ratio) at time  $t$  of the particles in the ensemble which reside in the cell  $\mathbf{x}$  on the sublattice  $\lambda$ . With above definition of  $\mathbf{K}$  the temporal derivative of the concentration  $c$  can now be written as

$$(\dot{c}(\cdot, t))_\lambda = \sum_{\mu} (\mathbf{K}(\cdot))_{\lambda,\mu} * (c(\cdot, t))_\mu, \quad (2.2.3)$$

where the symbol  $*$  denotes convolution in space. This now explains where  $\mathbf{K}$  got its symbol: it is the matrix-valued diffusion kernel.

Just as such equations are customarily solved I apply the element-wise spatial Fourier transformation, that means  $\mathcal{F}((c(\cdot, t))_\lambda) = (\hat{c}(\cdot, t))_\lambda$  analogously for  $\mathbf{K}$ :

$$(\hat{\dot{c}}(\mathbf{q}, t))_\lambda = \sum_{\mu} (\hat{\mathbf{K}}(\mathbf{q}))_{\lambda,\mu} \cdot (\hat{c}(\mathbf{q}, t))_\mu, \quad (2.2.4)$$

or put more elegantly

$$\hat{\dot{c}}(\mathbf{q}, t) = \hat{\mathbf{K}}(\mathbf{q}) \cdot \hat{c}(\mathbf{q}, t), \quad (2.2.5)$$

understood as matrix multiplication. An equation like that is one of the first problems encountered in the analysis of ordinary differential equations. Defining exponentiation for matrices via the series expansion of the scalar-valued exponential function, the solution to this ordinary differential can be immediately given:

$$\hat{c}(\mathbf{q}, t) = e^{\hat{\mathbf{K}}(\mathbf{q})t} \cdot \hat{c}(\mathbf{q}, 0). \quad (2.2.6)$$

Remembering that the vector notation of the concentration is just a shorthand for a scalar-valued concentration of the form  $\sum_{\lambda} (c(\cdot, t))_{\lambda} * \delta(\cdot - \mathbf{r}_{\lambda})$ , its Fourier transform is therefore  $\sum_{\lambda} (\hat{c}(\cdot, t))_{\lambda} \exp(-i\mathbf{q}\mathbf{r}_{\lambda})$ .

Let now  $f_{\mu}^{\lambda}(\Delta\mathbf{x}, \Delta t)$  be the probability distribution for finding a particle at time  $\Delta t$  on the site  $\mu$  of cell  $\Delta\mathbf{x}$  if it was at time 0 at site  $\lambda$  of cell  $\mathbf{o}$ . The spatial Fourier transform of this function is  $(e^{\hat{\mathbf{K}}(\mathbf{q})\Delta t})_{\mu, \lambda}$  (use Eq. 2.2.6 with an initial condition  $c$  equal to 1 at site  $\mathbf{o}$  and sublattice  $\lambda$  and take entry  $\mu$  of the result). Just considering the particles from sublattice  $\lambda$  would give for the self-correlation function  $\sum_{\mu} f_{\mu}^{\lambda}(\mathbf{x} - \mathbf{r}_{\mu} + \mathbf{r}_{\lambda}, \Delta t)$ . Taking into account the particles starting from all sublattices with their respective weights  $p_{\lambda}$  gives

$$G_s(\Delta\mathbf{x}, \Delta t) = \sum_{\mu} \sum_{\lambda} f_{\mu}^{\lambda}(\Delta\mathbf{x} - \mathbf{r}_{\mu} + \mathbf{r}_{\lambda}, \Delta t) p_{\lambda}, \quad (2.2.7)$$

and in the Fourier domain

$$I_s(\mathbf{q}, \Delta t) := \mathcal{F}(G_s(\cdot, \Delta t))(\mathbf{q}) = \sum_{\mu} e^{-i\mathbf{q}\mathbf{r}_{\mu}} \sum_{\lambda} (e^{\hat{\mathbf{K}}(\mathbf{q})\Delta t})_{\mu, \lambda} p_{\lambda} e^{i\mathbf{q}\mathbf{r}_{\lambda}}. \quad (2.2.8)$$

For reasons that will become clear in Sect. 3.4,  $I_s$  goes under the name incoherent intermediate scattering function.

To put Eq. 2.2.8 more elegantly, I first define the  $1 \times \Lambda$ -matrix  $\mathbf{E} = (e^{-i\mathbf{q}\mathbf{r}_1} \dots e^{-i\mathbf{q}\mathbf{r}_{\Lambda}})$ , the  $\Lambda \times \Lambda$ -diagonal matrix  $\mathbf{P}$  with the entries  $p_1 \dots p_{\Lambda}$  in the diagonal, and the Hermitized diffusion kernel in reciprocal space

$$\mathbf{K}'(\mathbf{q}) := \sqrt{\mathbf{P}^{-1}} \hat{\mathbf{K}}(\mathbf{q}) \sqrt{\mathbf{P}}. \quad (2.2.9)$$

Because each component of  $\mathbf{K}(\Delta\mathbf{x})$  is real, taking the component-wise complex conjugation of its Fourier transform is equivalent to inverting the independent variable:

$$\hat{\mathbf{K}}(-\mathbf{q}) = \overline{\hat{\mathbf{K}}(\mathbf{q})}. \quad (2.2.10)$$

To show that  $\mathbf{K}'(\mathbf{q})$  is actually Hermitian I first restate Eq. 2.2.2:

$$\mathbf{K}(\Delta\mathbf{x})\mathbf{P} = (\mathbf{K}(-\Delta\mathbf{x})\mathbf{P})^T = \mathbf{P}\mathbf{K}^T(-\Delta\mathbf{x}), \quad (2.2.11)$$

which naturally also holds for its Fourier transform

$$\hat{\mathbf{K}}(\mathbf{q})\mathbf{P} = \mathbf{P}\hat{\mathbf{K}}^T(-\mathbf{q}). \quad (2.2.12)$$

Multiplying this equality from both sides by  $\sqrt{\mathbf{P}^{-1}}$  and using Eq. 2.2.10 leads to

$$\sqrt{\mathbf{P}^{-1}}\hat{\mathbf{K}}(\mathbf{q})\sqrt{\mathbf{P}} = \sqrt{\mathbf{P}}\hat{\mathbf{K}}^T(-\mathbf{q})\sqrt{\mathbf{P}^{-1}} = \sqrt{\mathbf{P}}\hat{\mathbf{K}}^*(\mathbf{q})\sqrt{\mathbf{P}^{-1}}, \quad (2.2.13)$$

where  $(\dots)^*$  denotes the adjoint matrix, thereby proving the claim.

With these definitions Eq. 2.2.8 reads

$$\begin{aligned} I_s(\mathbf{q}, \Delta t) &= \mathbf{E}(\mathbf{q}) \exp(\hat{\mathbf{K}}(\mathbf{q})\Delta t) \mathbf{P} \mathbf{E}^*(\mathbf{q}) = \mathbf{E}(\mathbf{q}) \exp\left(\sqrt{\mathbf{P}}\hat{\mathbf{K}}'(\mathbf{q})\sqrt{\mathbf{P}^{-1}}\Delta t\right) \mathbf{P} \mathbf{E}^*(\mathbf{q}) \\ &= \mathbf{E}(\mathbf{q})\sqrt{\mathbf{P}} \exp(\mathbf{K}'(\mathbf{q})\Delta t) \sqrt{\mathbf{P}} \mathbf{E}^*(\mathbf{q}). \end{aligned} \quad (2.2.14)$$

From

$$\begin{aligned} \overline{I_s(\mathbf{q}, \Delta t)} &= I_s(\mathbf{q}, \Delta t)^* = \left(\mathbf{E}(\mathbf{q})\sqrt{\mathbf{P}} \exp(\mathbf{K}'(\mathbf{q})\Delta t) \sqrt{\mathbf{P}} \mathbf{E}^*(\mathbf{q})\right)^* \\ &= \mathbf{E}^{**}(\mathbf{q})\sqrt{\mathbf{P}^*} \exp(\mathbf{K}'^*(\mathbf{q})\Delta t) \sqrt{\mathbf{P}^*} \mathbf{E}^*(\mathbf{q}) \\ &= \mathbf{E}(\mathbf{q})\sqrt{\mathbf{P}} \exp(\mathbf{K}'(\mathbf{q})\Delta t) \sqrt{\mathbf{P}} \mathbf{E}^*(\mathbf{q}) \\ &= I_s(\mathbf{q}, \Delta t), \end{aligned} \quad (2.2.15)$$

where the first equality followed trivially from considering  $I_s$  an  $1 \times 1$ -matrix and the following equalities from the Hermitianness of  $\mathbf{K}'$  and the rules for matrix transposition, it follows that  $I_s$  is real. Using this fact, Eq. 2.2.10 and the definition of  $\mathbf{E}(\mathbf{q})$

$$I_s(\mathbf{q}, \Delta t) = \overline{I_s(\mathbf{q}, \Delta t)} = \mathbf{E}(-\mathbf{q})\sqrt{\mathbf{P}} \exp(\mathbf{K}'(-\mathbf{q})\Delta t) \sqrt{\mathbf{P}} \mathbf{E}^*(-\mathbf{q}) = I_s(-\mathbf{q}, \Delta t), \quad (2.2.16)$$

so  $I_s$  is in fact even and real-valued. Therefore also  $G_s$ , being the back-transform of an real-valued even function, is even (and real-valued).

This is at first glance surprising, as the lattice's being composed of sublattices will in the general case destroy the inversion symmetry of the underlying Bravais lattice. The key point in above derivation, however, was the invocation of detailed balance. This principle just says that the same number of atoms hop from site  $A$  to site  $B$  as from site  $B$  to site  $A$ , so even if the fluxes exiting site  $A$  have no inversion symmetry, the other sites make up for that imbalance, leading to an even correlation function.

It is instructive to write  $I_s$  in yet another way. Diagonalizing  $\mathbf{K}'$ , i.e. writing

$$\mathbf{K}'(\mathbf{q}) = \mathbf{V}(\mathbf{q})\mathbf{D}(\mathbf{q})\mathbf{V}^*(\mathbf{q}), \quad (2.2.17)$$

with  $\mathbf{V}(\mathbf{q})$  a unitary matrix and  $\mathbf{D}(\mathbf{q})$  a diagonal matrix with real (because  $\mathbf{K}'$  is Hermitian) non-positive (see Sect. A.1) diagonal entries, Eq. 2.2.14 reads

$$\begin{aligned}
I_s(\mathbf{q}, \Delta t) &= \mathbf{E}(\mathbf{q}) \sqrt{\mathbf{P}} \exp(\mathbf{V}(\mathbf{q}) \mathbf{D}(\mathbf{q}) \mathbf{V}^*(\mathbf{q}) \Delta t) \sqrt{\mathbf{P}} \mathbf{E}^*(\mathbf{q}) \\
&= \mathbf{E}(\mathbf{q}) \sqrt{\mathbf{P}} \mathbf{V}(\mathbf{q}) \exp(\mathbf{D}(\mathbf{q}) \Delta t) \mathbf{V}^*(\mathbf{q}) \sqrt{\mathbf{P}} \mathbf{E}^*(\mathbf{q}) \\
&= \sum_{\lambda} e^{(\mathbf{D}(\mathbf{q}))_{\lambda, \lambda} \Delta t} \left| \sum_{\mu} e^{-i\mathbf{q} \mathbf{r}_{\mu}} \sqrt{p_{\mu}} (\mathbf{V}(\mathbf{q}))_{\mu, \lambda} \right|^2. \tag{2.2.18}
\end{aligned}$$

$I_s(\mathbf{q}, \Delta t)$  for a fixed  $\mathbf{q}$  is therefore a sum of  $\Lambda$  (possibly degenerate) exponential decays, where the respective decay times are given by the inverse of the diagonal entries in  $\mathbf{D}(\mathbf{q})$  and the respective weights are a function of the occupation probabilities of the sublattices  $p_{\lambda}$ , the geometry within the unit cell  $\mathbf{r}_{\lambda}$  in relation to  $\mathbf{q}$ , and the jump frequencies between the various sites.

I want to point out an analogy of the present problem to another one most solid state physicists are probably more familiar with: phonon dispersion. In a crystal composed of  $\Lambda$  sublattices there are  $\Lambda$  phonon states for a given wave-vector  $\mathbf{q}$ , one acoustic and  $\Lambda - 1$  optical phonons. The eigenvalues of  $\mathbf{K}'(\mathbf{q})$  (which are the diagonal entries of  $\mathbf{D}(\mathbf{q})$ ) behave similarly: for small  $\mathbf{q}$  they can be divided into one value describing the decay of long-range correlations and  $\Lambda - 1$  values describing the fluxes between the sublattices. Considerations along the lines of the proof in Sect. A.1 show that the appearance of an additional eigenvalue equal to zero at a  $\mathbf{q}$  equal to a reciprocal lattice vector (apart from the “acoustic” eigenvalue) is equivalent to the lattice’s decomposing into two (or more) systems of sublattices, so that there is no flux from sites in one system to sites in the other (in the phonon analogy this would correspond to the artificial example of two interleaved lattices which do not interact, leading to an optical phonon branch behaving like an additional acoustic branch). A non-trivial case is the interstitialcy mechanism of diffusion in the diamond lattice, see Sect. 4.1. In this case there is no flux between the two sublattices, so for a  $\mathbf{q}$  equal to a reciprocal lattice vector the intermediate incoherent scattering function does not decay in time.

I want to treat now Eq. 2.2.18 in the limit of small  $\mathbf{q}$  for the non-degenerate case, i.e. where the lattice does not decompose. Using Eq. 2.2.1 it follows that the diagonal vector of  $\sqrt{\mathbf{P}}$ , in the following denoted  $\sqrt{\mathbf{p}}$ , is the “acoustic” eigenvector of  $\mathbf{K}'(\mathbf{o})$  corresponding to the eigenvalue 0. As  $\sqrt{\mathbf{P}} \mathbf{E}^*(\mathbf{q})$  converges to  $\sqrt{\mathbf{p}}$  for  $\mathbf{q} \rightarrow \mathbf{o}$ , the weight of the “optical” decays in Eq. 2.2.18 vanishes, leaving only the “acoustic” decay, the eigenvalue of which goes to 0. For computing the behaviour at small  $\mathbf{q}$  of this eigenvalue, in the following denoted  $d(\mathbf{q})$  and defined by the equation

$$d(\mathbf{q}) \mathbf{v}(\mathbf{q}) = \mathbf{K}'(\mathbf{q}) \mathbf{v}(\mathbf{q}), \tag{2.2.19}$$

I write the relevant quantities as power series in  $\mathbf{q}$ :

$$\begin{aligned}
d(\mathbf{q}) &= d^0 + d^1(\mathbf{q}) + d^2(\mathbf{q}) + O(q^3), \\
\mathbf{v}(\mathbf{q}) &= \mathbf{v}^0 + \mathbf{v}^1(\mathbf{q}) + \mathbf{v}^2(\mathbf{q}) + O(q^3), \\
\mathbf{K}'(\mathbf{q}) &= \sqrt{\mathbf{P}^{-1}} (\mathbf{K}^0 + \mathbf{K}^1(\mathbf{q}) + \mathbf{K}^2(\mathbf{q})) \sqrt{\mathbf{P}} + O(q^3). \tag{2.2.20}
\end{aligned}$$

Here quantities with 1 in the exponent are linear functions of  $\mathbf{q}$  and quantities with 2 are bilinear functions. Expanding in a power series is valid because in the

non-degenerate case  $d(\mathbf{q})$  has a multiplicity of 1 everywhere around  $\mathbf{q} = \mathbf{0}$  and is therefore an analytical function of the coefficients of the characteristic polynomial of  $\mathbf{K}'(\mathbf{q})$ . By construction  $d^0$  is 0 and  $\mathbf{v}^0$  is  $\sqrt{\mathbf{p}}$ , but also  $d^1$  is 0 because  $\mathbf{K}'(\mathbf{q})$  and therefore also its eigenvalues are even functions in  $\mathbf{q}$ . This leads to the necessity for the linear terms in  $\mathbf{q}$  on the right-hand side of Eq. 2.2.19 to cancel for all  $\mathbf{q}$ , therefore

$$\mathbf{K}^1(\mathbf{q})\mathbf{p} + \mathbf{K}^0\sqrt{\mathbf{p}}\mathbf{v}^1 = 0. \quad (2.2.21)$$

$\mathbf{K}^0$  is not invertible, so  $\sqrt{\mathbf{p}}\mathbf{v}^1$  is given by

$$\sqrt{\mathbf{p}}\mathbf{v}^1 = -(\mathbf{K}^0)^{-1}\mathbf{K}^1(\mathbf{q})\mathbf{p} + s\mathbf{p}. \quad (2.2.22)$$

Here  $(\mathbf{K}^0)^{-1}$  denotes the Moore-Penrose pseudoinverse of  $\mathbf{K}^0$  and  $s\mathbf{p}$  spans the kernel of  $\mathbf{K}^0$  due to Eqs. 2.2.1 and 2.2.2 and the fact that the rank of the kernel is 1.

The quantity of interest  $d(\mathbf{q})$  follows then as

$$\begin{aligned} d(\mathbf{q}) &= \mathbf{v}(\mathbf{q})^T d_a(\mathbf{q}) \mathbf{v}(\mathbf{q}) = \mathbf{v}(\mathbf{q})^T \mathbf{K}'(\mathbf{q}) \mathbf{K}(\mathbf{q}) \\ &= \mathbf{v}(\mathbf{q})^T \sqrt{\mathbf{P}^{-1}} \left( \mathbf{K}^2 \sqrt{\mathbf{P}} \mathbf{v}^0 + \mathbf{K}^1 \sqrt{\mathbf{P}} \mathbf{v}^1 + \mathbf{K}^0 \sqrt{\mathbf{P}} \mathbf{v}^2 \right) + O(q^3) \\ &= \mathbf{e} \left( \mathbf{K}^2 \sqrt{\mathbf{P}} \mathbf{v}^0 + \mathbf{K}^1 \sqrt{\mathbf{P}} \mathbf{v}^1 \right) + O(q^3) \\ &= \mathbf{e} \left( \mathbf{K}^2(\mathbf{q}) - \mathbf{K}^1(\mathbf{q})(\mathbf{K}^0)^{-1}\mathbf{K}^1(\mathbf{q}) \right) \mathbf{p} + O(q^3) \end{aligned} \quad (2.2.23)$$

with  $\mathbf{e} = (1, \dots, 1)$  and observing the cancellation of various terms. The relevant matrices are explicitly given by

$$\begin{aligned} \mathbf{K}^0 &= \sum_{\Delta \mathbf{x}} \mathbf{K}(\Delta \mathbf{x}), \\ \mathbf{K}^1(\mathbf{q}) &= -i \sum_{\Delta \mathbf{x}} (q \Delta \mathbf{x}) \mathbf{K}(\Delta \mathbf{x}), \\ \mathbf{K}^2(\mathbf{q}) &= - \sum_{\Delta \mathbf{x}} \frac{(q \Delta \mathbf{x})^2}{2} \mathbf{K}(\Delta \mathbf{x}), \end{aligned} \quad (2.2.24)$$

so Eq. 2.2.23 is a non-negative (see Sect. A.1) quadratic form for small  $\mathbf{q}$

$$d(\mathbf{q}) = \mathbf{q}^T \mathbf{D} \mathbf{q} + O(q^3), \quad (2.2.25)$$

and the intermediate incoherent scattering function Eq. 2.2.18 reads for small  $\mathbf{q}$

$$I_s(\mathbf{q}, \Delta t) = e^{-\mathbf{q}^T \mathbf{D} \mathbf{q} \Delta t}. \quad (2.2.26)$$

The description of diffusion in macroscopic terms is given by Fick's laws. In Fick's first law the diffusion tensor  $\mathbf{D}$  is defined via the phenomenological linear relation between concentration gradient and mass flux

$$\mathbf{j} = -\mathbf{D}\nabla c. \quad (2.2.27)$$

Invoking mass conservation leads to Fick's second law

$$\dot{c} = \nabla \mathbf{D} \nabla c, \quad (2.2.28)$$

or in reciprocal space

$$\dot{\hat{c}}(\mathbf{q}, t) = -\mathbf{q} \mathbf{D} \mathbf{q} \hat{c}(\mathbf{q}, t). \quad (2.2.29)$$

Solving this equation with a delta distribution as initial condition gives

$$\hat{c}(\mathbf{q}, t) = e^{-\mathbf{q}^T \mathbf{D} \mathbf{q} t}. \quad (2.2.30)$$

Therefore the quadratic form  $\mathbf{D}$  describing the behaviour of the intermediate incoherent scattering function in Eq. 2.2.26 at small  $\mathbf{q}$  is nothing else than the macroscopic diffusion tensor. It is given by the macroscopic limit of the self-correlation function which is experimentally mainly determined from the spreading of a small amount of radioactive tracer atoms, so it is customarily called the tracer diffusion tensor.

In the degenerate case, where the lattice decomposes into mutually disconnected sets of sublattices, the problem can be solved on each set alone. Note that this can give different quadratic forms  $\mathbf{D}$  for the distinct sets of sublattice. Therefore the non-degeneracy assumption in the derivation of Eq. 2.2.26 is not just for convenience, in fact in the general case the macroscopic description by Fick's laws is not valid. For the above-mentioned case of interstitialcy diffusion in the diamond lattice both sublattices behave equally at small  $\mathbf{q}$ , so the partial intermediate incoherent scattering functions can be merged and the phenomenological macroscopic behaviour is recovered.

In the special case where the particles sit on a Bravais lattice and therefore all sites are equivalent, the diffusion kernel  $K(\Delta \mathbf{x})$  is scalar-valued, has inversion symmetry and  $\sum_{\Delta \mathbf{x}} K(\Delta \mathbf{x}) = 0$ . Defining

$$\begin{aligned} \Gamma_{\text{inc}}(\mathbf{q}) &= -\hat{K}(\mathbf{q}) = -\mathcal{F}(K)(\mathbf{q}) = -\sum_{\Delta \mathbf{x}} K(\Delta \mathbf{x}) \cos(\mathbf{q} \Delta \mathbf{x}) \\ &= \sum_{\Delta \mathbf{x}} K(\Delta \mathbf{x}) (1 - \cos(\mathbf{q} \Delta \mathbf{x})), \end{aligned} \quad (2.2.31)$$

Eq. 2.2.18 has the concise form

$$I_s(\mathbf{q}, \Delta t) = e^{-\Gamma_{\text{inc}}(\mathbf{q}) \Delta t}. \quad (2.2.32)$$

$\Gamma_{\text{inc}}$  is called the incoherent linewidth, as quasi-elastic methods measure it as a line broadening (see Sect. 3.1). In the Bravais case Eq. 2.2.23 and equivalently Eq. 2.2.31 simplify to

$$d(\mathbf{q}) = \Gamma_{\text{inc}}(\mathbf{q}) = \sum_{\Delta \mathbf{x}} K(\Delta \mathbf{x}) \frac{(\mathbf{q} \Delta \mathbf{x})^2}{2} \quad (2.2.33)$$



for small  $\mathbf{q}$ . Additionally invoking cubic symmetry leads to the ellipsoid described by the quadratic form  $\mathbf{D}$  becoming a sphere, therefore diffusion becomes isotropic, completely specified by the scalar-valued tracer diffusion constant  $D$  with

$$D = \sum_{\Delta\mathbf{x}} K(\Delta\mathbf{x}) \frac{|\Delta\mathbf{x}|^2}{6}. \quad (2.2.34)$$

This equation is called the Einstein relation, where the additional factor 3 in the denominator compared to Eq. 2.2.33 is due to the value of  $(\mathbf{q}\Delta\mathbf{x})^2$  averaged over all directions being

$$\langle (\mathbf{q}\Delta\mathbf{x})^2 \rangle = \frac{|\mathbf{q}|^2 |\Delta\mathbf{x}|^2}{3}. \quad (2.2.35)$$

It is worth reflecting on the approximations inherent in this section's considerations. First, in actual metallic systems in most cases diffusion does not happen by spontaneous, unprovoked hopping, rather it is the result of the migration of a vacancy. This fact leads to correlations between hopping events. These correlations can, however, be satisfactorily incorporated into the model in the framework of the so-called encounter model (see Sect. 3.5). The second issue, the influence of the particle's surroundings, was already addressed at the beginning of this section. With interacting particles the jump probabilities are not a strict function of the initial and target sublattices, but they vary with the surroundings. This leads to the fact that there is not one single well-defined decay time per sublattice, so the decay gets "stretched" due to averaging over the distinct surroundings, corresponding to different exponential decays. Still, in most experimental studies this effect is not drastic, and the data can be fitted by one exponential per sublattice.

## 2.3 The Pair-Correlation Function

This section gives an analytic theory of the pair-correlation function in the case of short-range order on the lattice. The simplification introduced in Sect. 2.2, i.e. describing the systems in the ensemble only by the position of the tagged particle and accounting for the different surroundings only through an average "effective" surrounding, does not work here, as the very essence of the pair correlation function lies in the correlation with *other* particles. Therefore the temporal evolution of the positions of all the particles in the system has to be described in a unified approach, explicitly treating the correlations. Nevertheless, in order to obtain analytic results, some approximations have to be made, namely the high-temperature limit, i.e. to treat correlations due to the energetics as first-order perturbations. A further assumption is that the Hamiltonian is given via pairwise interactions. Considering several sublattices would only obfuscate the ideas presented here, so I assume the particles to sit on sites of a Bravais lattice. The derivation presented here, which uses classical

transition state theory [13], leads to the same results as the one given by Sinha and Ross [11] set in a general framework of lattice dynamics. In the meantime it has been published as Leitner and Vogl [8]. For a still quicker, although less fundamental treatment of this problem see the last paragraphs of this section.

A state of the system is described by the occupation function  $\sigma$ , that is,  $\sigma(\mathbf{x}) = 1$  if the site  $\mathbf{x}$  is occupied by a particle and  $\sigma(\mathbf{x}) = 0$  if not. The most general Hamiltonian for pair potentials is given by

$$H(\sigma) = V_0 + V_1 \sum_{\mathbf{x}} \sigma(\mathbf{x}) + \sum_{\mathbf{x}, \mathbf{y}} V(\mathbf{x} - \mathbf{y}) \sigma(\mathbf{x}) \sigma(\mathbf{y}). \quad (2.3.1)$$

In the following only the differences between energies of states in the canonical ensemble will be required, so the expression

$$H'(\sigma) = \sum_{\mathbf{x}, \mathbf{y}} V(\mathbf{x} - \mathbf{y}) \sigma(\mathbf{x}) \sigma(\mathbf{y}) \quad (2.3.2)$$

can be used without loss of generality. I write

$$\Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma) = H'(\sigma_2) - H'(\sigma_1) \quad (2.3.3)$$

for the difference in energy between a state  $\sigma_1$  with

$$\sigma_1(\mathbf{y}) = \begin{cases} 1 & \mathbf{y} = \mathbf{x} \\ 0 & \mathbf{y} = \mathbf{x} + \Delta \mathbf{x} \\ \sigma(\mathbf{y}) & \text{else} \end{cases} \quad (2.3.4)$$

and a state  $\sigma_2$  with

$$\sigma_2(\mathbf{y}) = \begin{cases} 0 & \mathbf{y} = \mathbf{x} \\ 1 & \mathbf{y} = \mathbf{x} + \Delta \mathbf{x} \\ \sigma(\mathbf{y}) & \text{else.} \end{cases} \quad (2.3.5)$$

Described in words,  $\Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma)$  is the energy gained (or lost) when moving a particle from  $\mathbf{x}$  to  $\mathbf{x} + \Delta \mathbf{x}$  in the environment specified by  $\sigma$ . I write  $E_s(\mathbf{x}, \mathbf{x} + \Delta \mathbf{x}; \sigma)$  for the energy of the saddle point in the energy landscape on the path from  $\mathbf{x}$  to  $\Delta \mathbf{x}$ , relative to the average of the initial and final energy  $H'(\sigma_1)$  and  $H'(\sigma_2)$ . Equivalently stated, the energy necessary to invest for raising a particle on its way from  $\mathbf{x}$  to  $\Delta \mathbf{x}$  onto the saddle point is given by  $E_s(\mathbf{x}, \mathbf{x} + \Delta \mathbf{x}; \sigma) + \Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma)/2$ , for moving it back it is  $E_s(\mathbf{x}, \mathbf{x} + \Delta \mathbf{x}; \sigma) - \Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma)/2$ . These concepts will become more clear by means of an example in Sect. 4.3.

There are two equivalent possible choices for the fundamental dynamic process: either the particles hop into empty sites (and do not hop if the prospective target site is occupied) or the occupancy of two sites is exchanged, i.e. if exactly one of the two is occupied, after the exchange the other is occupied, if either both are occupied or both are unoccupied, nothing changes. I use the latter concept, as it is symmetric

under the operation  $\sigma \rightarrow 1 - \sigma$ . The rate of exchanges of the occupancies of  $\mathbf{x}$  and  $\mathbf{x} + \Delta\mathbf{x}$  can then be written

$$\begin{aligned}\omega &= \nu_{\Delta\mathbf{x}} e^{-\frac{\Delta E(\mathbf{x}; \Delta\mathbf{x}, \sigma)}{2k_B T}} e^{-\frac{E_s(\mathbf{x}, \mathbf{x} + \Delta\mathbf{x}; \sigma)}{k_B T}} \\ &= \nu_{\Delta\mathbf{x}} e^{-\frac{E_s(\Delta\mathbf{x})}{k_B T}} e^{-\frac{\Delta E(\mathbf{x}; \Delta\mathbf{x}, \sigma)}{2k_B T}} e^{-\frac{\Delta E_s(\mathbf{x}, \mathbf{x} + \Delta\mathbf{x}; \sigma)}{k_B T}},\end{aligned}\quad (2.3.6)$$

where  $E_s(\Delta\mathbf{x})$  is the mean saddle point energy for a jump along  $\Delta\mathbf{x}$  with  $\Delta E_s(\mathbf{x}, \mathbf{x} + \Delta\mathbf{x}; \sigma)$  being the variations around this mean value and  $\nu_{\Delta\mathbf{x}}$  the attempt frequency for such a jump [13].

I will now treat the temporal evolution of the system, where the system is initially in the state  $\sigma$ . Obviously a given site  $\mathbf{x}$  can either be occupied or unoccupied, so  $\sigma(\mathbf{x})$  is either 0 or 1. It will turn out that the equation describing the evolution is in first order linear in  $\sigma$ , therefore the same relationship holds also for the expected value, that is the average value over an ensemble of systems. The reader is invited to choose the most convenient setting, either a concrete state and transition probabilities or expected values and their temporal evolution.

$$\begin{aligned}\dot{\sigma}(\mathbf{x}) &= \sum_{\Delta\mathbf{x}} \left( \sigma(\mathbf{x} + \Delta\mathbf{x})(1 - \sigma(\mathbf{x})) e^{\frac{\Delta E(\mathbf{x}; \Delta\mathbf{x}, \sigma)}{2k_B T}} \right. \\ &\quad \left. - \sigma(\mathbf{x})(1 - \sigma(\mathbf{x} + \Delta\mathbf{x})) e^{-\frac{\Delta E(\mathbf{x}; \Delta\mathbf{x}, \sigma)}{2k_B T}} \right) \nu_{\Delta\mathbf{x}} e^{-\frac{E_s(\mathbf{x}, \mathbf{x} + \Delta\mathbf{x}; \sigma)}{k_B T}} \\ &= \sum_{\Delta\mathbf{x}} \nu_{\Delta\mathbf{x}} e^{-\frac{E_s(\Delta\mathbf{x})}{k_B T}} e^{-\frac{\Delta E_s(\mathbf{x}, \mathbf{x} + \Delta\mathbf{x}; \sigma)}{k_B T}} \\ &\quad \times \left( \sigma(\mathbf{x} + \Delta\mathbf{x})(1 - \sigma(\mathbf{x})) e^{\frac{\Delta E(\mathbf{x}; \Delta\mathbf{x}, \sigma)}{2k_B T}} \right. \\ &\quad \left. - \sigma(\mathbf{x})(1 - \sigma(\mathbf{x} + \Delta\mathbf{x})) e^{-\frac{\Delta E(\mathbf{x}; \Delta\mathbf{x}, \sigma)}{2k_B T}} \right) \\ &= \sum_{\Delta\mathbf{x}} \tilde{\nu}_{\Delta\mathbf{x}} \left( (\sigma(\mathbf{x} + \Delta\mathbf{x}) - \sigma(\mathbf{x})) \left( 1 - \frac{\Delta E_s(\mathbf{x}, \mathbf{x} + \Delta\mathbf{x}; \sigma)}{k_B T} \right) \right. \\ &\quad \left. + \frac{\Delta E(\mathbf{x}; \Delta\mathbf{x}, \sigma)}{2k_B T} (\sigma(\mathbf{x}) + \sigma(\mathbf{x} + \Delta\mathbf{x})) \right. \\ &\quad \left. - 2\sigma(\mathbf{x})\sigma(\mathbf{x} + \Delta\mathbf{x}) + O\left((E/k_B T)^2\right) \right)\end{aligned}\quad (2.3.7)$$

Here  $E$  is a measure for the typical energy variations, in both the saddle point and the stable positions, i.e.  $\Delta E(\mathbf{x}; \Delta\mathbf{x}, \sigma) = O(E)$  and  $\Delta E_s(\mathbf{x}, \mathbf{x} + \Delta\mathbf{x}; \sigma) = O(E)$ .  $\tilde{\nu}_{\Delta\mathbf{x}} = \nu_{\Delta\mathbf{x}} \exp(-E_s(\Delta\mathbf{x})/k_B T)$  is the raw jump frequency neglecting the influence of energy and correlations.

The system is assumed to be only short-range ordered, this means that

$$\langle \sigma(\mathbf{x})\sigma(\mathbf{y}) \rangle - \langle \sigma(\mathbf{x}) \rangle \langle \sigma(\mathbf{y}) \rangle = O(E/k_B T) \quad (2.3.8)$$

for  $\mathbf{x} \neq \mathbf{y}$ . As both  $\Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma)$  and  $\Delta E_s(\mathbf{x}, \mathbf{x} + \Delta \mathbf{x}; \sigma)$  are linear functionals with respect to  $\sigma$  which depend neither on  $\sigma(\mathbf{x})$  nor on  $\sigma(\mathbf{x} + \Delta \mathbf{x})$ , it follows that

$$\langle \Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma) \sigma(\mathbf{x}) \rangle - \langle \Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma) \rangle \langle \sigma(\mathbf{x}) \rangle = O\left((E/k_B T)^2\right), \quad (2.3.9)$$

analogously for similar quantities. Applying this to Eq. 2.3.7 and cancelling (noting that  $\langle \sigma(\mathbf{x}) \rangle$  is equal to the concentration of particles  $c$ ) shows that

$$\dot{\sigma}(\mathbf{x}) = \sum_{\Delta \mathbf{x}} \tilde{v}_{\Delta \mathbf{x}} \left( \sigma(\mathbf{x} + \Delta \mathbf{x}) - \sigma(\mathbf{x}) + \frac{\Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma)}{k_B T} c(1 - c) \right) \quad (2.3.10)$$

in first order approximation, in particular the influence of the configuration on the energetics of the saddle point vanishes, only the energies of the initial and the final state matter.

Going back to Eq. 2.3.2,  $\Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma)$  is explicitly given by

$$\begin{aligned} \Delta E(\mathbf{x}; \Delta \mathbf{x}, \sigma) &= \sum_{\mathbf{y}} V(\mathbf{x} + \Delta \mathbf{x} - \mathbf{y}) \sigma(\mathbf{y}) - \sum_{\mathbf{y}} V(\mathbf{x} - \mathbf{y}) \sigma(\mathbf{y}) \\ &= \sum_{\mathbf{z}} V(\mathbf{z}) (\sigma(\mathbf{x} + \Delta \mathbf{x} - \mathbf{z}) - \sigma(\mathbf{x} - \mathbf{z})). \end{aligned} \quad (2.3.11)$$

Defining the amplitude  $A = \mathcal{F}(\sigma)$  and using basic results about the Fourier transform of convolutions, the transform in  $\mathbf{x}$  of above equation reads

$$\mathcal{F}(\Delta E(., \Delta \mathbf{x}, \sigma))(\mathbf{q}) = \hat{V}(\mathbf{q}) A(\mathbf{q}) (e^{i\mathbf{q} \Delta \mathbf{x}} - 1), \quad (2.3.12)$$

where  $\hat{V}$  is the transform of the pair potential  $V$ . Using this result the Fourier transform of Eq. 2.3.10 can be given as

$$\begin{aligned} \dot{A}(\mathbf{q}) &= \sum_{\Delta \mathbf{x}} \tilde{v}_{\Delta \mathbf{x}} \left( A(\mathbf{q}) e^{i\mathbf{q} \Delta \mathbf{x}} - A(\mathbf{q}) + \frac{\hat{V}(\mathbf{q}) A(\mathbf{q}) (e^{i\mathbf{q} \Delta \mathbf{x}} - 1)}{k_B T} c(1 - c) \right) \\ &= A(\mathbf{q}) \sum_{\Delta \mathbf{x}} \tilde{v}_{\Delta \mathbf{x}} (\cos(\mathbf{q} \Delta \mathbf{x}) - 1) \left( 1 + \frac{\hat{V}(\mathbf{q}) c(1 - c)}{k_B T} \right). \end{aligned} \quad (2.3.13)$$

In this section's nomenclatura  $\Gamma_{\text{inc}}$  now reads (cp. Eq. 2.2.31)

$$\Gamma_{\text{inc}}(\mathbf{q}) = \sum_{\Delta \mathbf{x}} \tilde{v}_{\Delta \mathbf{x}} (1 - \cos(\mathbf{q} \Delta \mathbf{x})), \quad (2.3.14)$$

but this time the relevant quantity is the coherent linewidth

$$\Gamma_{\text{coh}}(\mathbf{q}) = \Gamma_{\text{inc}}(\mathbf{q}) \left( 1 + \frac{\hat{V}(\mathbf{q}) c(1 - c)}{k_B T} \right), \quad (2.3.15)$$

giving

$$\langle A(\mathbf{q}, t) \rangle = A(\mathbf{q}, 0) e^{-\Gamma_{\text{coh}}(\mathbf{q})t}. \quad (2.3.16)$$

Writing the time dependence of  $\sigma$  explicitly, the pair-correlation function  $G(\Delta\mathbf{x}, \Delta t)$  is defined by

$$G(\Delta\mathbf{x}, \Delta t) = \langle \sigma(., .) \sigma(. + \Delta\mathbf{x}, . + \Delta t) \rangle. \quad (2.3.17)$$

Note that

$$\begin{aligned} G(\Delta\mathbf{x}, \Delta t) &= \langle \sigma(., .) \sigma(. + \Delta\mathbf{x}, . + \Delta t) \rangle = \langle \sigma(. - \Delta\mathbf{x}, . - \Delta t) \sigma(., .) \rangle \\ &= \langle \sigma(., .) \sigma(. - \Delta\mathbf{x}, . - \Delta t) \rangle = G(-\Delta\mathbf{x}, -\Delta t). \end{aligned} \quad (2.3.18)$$

Due to time-inversion symmetry  $G$  is even in time, using this fact and above result it is also even in space.

Again using the interplay of Fourier transforming and convoluting the coherent intermediate scattering function is given by

$$\begin{aligned} I(\mathbf{q}, \Delta t) &:= \mathcal{F}(G(., \Delta t))(\mathbf{q}) = \langle A(\mathbf{q}, .) \hat{A}(\mathbf{q}, . + \Delta t) \rangle = \langle A(\mathbf{q} + .) \hat{A}(\mathbf{q}, .) e^{-\Gamma_{\text{coh}}(\mathbf{q})\Delta t} \rangle \\ &= I_{\text{SRO}}(\mathbf{q}) e^{-\Gamma_{\text{coh}}(\mathbf{q})\Delta t}. \end{aligned} \quad (2.3.19)$$

$I_{\text{SRO}}(\mathbf{q})$  is the expected value of the intensity, the squared modulus of the amplitude, due to short-range order, for a given  $\mathbf{q}$ .

In the framework of the approximations invoked here the intensity can be directly related to the potential via the Clapp-Moss-relations [3], see Sect. A.2:

$$I_{\text{SRO}}(\mathbf{q}) = \frac{1}{\left(1 + \frac{\hat{V}(\mathbf{q})c(1-c)}{kT}\right)}, \quad (2.3.20)$$

therefore

$$\Gamma_{\text{coh}}(\mathbf{q}) = \frac{\Gamma_{\text{inc}}(\mathbf{q})}{I_{\text{SRO}}(\mathbf{q})}. \quad (2.3.21)$$

The intensity  $I_{\text{SRO}}(\mathbf{q})$  is measured in Laue units, where one Laue unit is  $Nc(1 - c)$  with  $N$  the number of lattice sites (this is just the value of the configurational diffuse scattering of a random alloy). In particular it follows that the coherent linewidth is equal to the incoherent linewidth for vanishing interactions, and  $I_s = I$ .

Just as with the intermediate incoherent scattering function in Sect. 2.2 also here the behaviour of  $\Gamma_{\text{coh}}(\mathbf{q})$  for small  $\mathbf{q}$  is given by a quadratic form corresponding to a diffusion tensor  $\mathbf{D}$ . In this case, however, it describes the decay of chemical fluctuations in the macroscopic limit, I will therefore call it the chemical diffusion tensor (or chemical diffusion constant in the cubic case). An analogon of the Einstein relation also holds here, by Eq. 2.3.21 the diffusion constant is just the value of the tracer diffusion constant in Eq. 2.2.34 divided by  $I_{\text{SRO}}(\mathbf{0})$ .

The fact that the relaxation of fluctuations (i.e. the decay of the coherent intermediate scattering function) becomes slower than the value given by Chudley and Elloitt

[2] for positions in reciprocal space with high intensity has been known qualitatively under the name de Gennes-narrowing [5] from studies of liquids and colloidal glasses [1, 4]. It is not difficult to understand: a high  $I_{\text{SRO}}(\mathbf{q})$  means that the particles prefer to build local arrangements corresponding to a high Fourier component at  $\mathbf{q}$ . The reason can only be that such arrangements are energetically favoured compared to other arrangements, therefore it takes more energy to break such arrangements up, making them longer-lived. However, the fact that the decay is in the first approximation still a single exponential given by the very simple relation (2.3.21), being only a function of the static energetics, is not so obvious. The simulations in Sect. 4.3 elucidate what happens when the approximations invoked here break down.

I want also to sketch another, less fundamental way of deriving Eq. 2.3.21. I write the pair-correlation function as the sum of the self-correlation function and the distinct-correlation function

$$G(\Delta\mathbf{x}, \Delta t) = G_s(\Delta\mathbf{x}, \Delta t) + G_d(\Delta\mathbf{x}, \Delta t), \quad (2.3.22)$$

equivalently in reciprocal space

$$I(\mathbf{q}, \Delta t) = I_s(\mathbf{q}, \Delta t) + I_d(\mathbf{q}, \Delta t). \quad (2.3.23)$$

The behaviour of  $I_s(\mathbf{q}, \Delta t)$  was derived in Sect. 2.2, it decays with the rate  $\Gamma_{\text{inc}}(\mathbf{q})$ . The assumption of equilibrium leads to time-inversion symmetry, therefore Eq. 2.2.32 can be generalized to negative time differences

$$I_s(\mathbf{q}, \Delta t) = e^{-\Gamma_{\text{inc}}(\mathbf{q})|\Delta t|}. \quad (2.3.24)$$

$G_d(\Delta\mathbf{x}, \Delta t)$  and therefore  $I_d(\mathbf{q}, \Delta t)$  can be seen as the reaction of the surrounding particles to the occupation of site  $\mathbf{o}$ . This reaction happens via diffusion and will therefore vary smoothly in time, just as the heat conduction equation smoothes out singularities in the initial or boundary data.  $I_d(\mathbf{q}, \Delta t)$  obviously also has time-inversion symmetry, so with it being smooth everywhere it has a vanishing temporal derivative at  $\Delta t = 0$ . Therefore

$$-\Gamma_{\text{coh}}(\mathbf{q})I_{\text{SRO}}(\mathbf{q}) = \frac{d}{d\Delta t}I(\mathbf{q}, \Delta t)\big|_{\Delta t=0^+} = \frac{d}{d\Delta t}I_s(\mathbf{q}, \Delta t)\big|_{\Delta t=0^+} = -\Gamma_{\text{inc}}(\mathbf{q}), \quad (2.3.25)$$

and Eq. 2.3.21 follows.

## References

1. C. Caronna, Y. Chushkin, A. Madsen, A. Cupane, Dynamics of nanoparticles in a supercooled liquid. Phys. Rev. Lett. **100**, 055702 (2008)
2. C.T. Chudley, R.J. Elliott, Neutron scattering from a liquid on a jump diffusion model. Proc. Phys. Soc. Lond. **77**, 353 (1961)
3. P.C. Clapp, S.C. Moss, Correlation functions of disordered binary alloys. I. Phys. Rev. **142**, 418 (1966)

4. B.A. Dasannacharya, K.R. Rao, Neutron scattering from liquid argon. *Phys. Rev.* **137**, A417 (1965)
5. P.G. de Gennes, Liquid dynamics and inelastic scattering of neutrons. *Physica* **25**, 825 (1959)
6. M.A. Krivoglaz, The effect of diffusion on the scattering of neutrons and photons by crystal imperfections and on the Mössbauer effect. *Sov. Phys. JETP* **13**, 1273 (1961)
7. R. Kutner, I. Sosnowska, Thermal neutron scattering from a hydrogen-metal system in terms of a general multi-sublattice jump diffusion model—I: theory. *J. Phys. Chem. Solids* **38**, 741 (1977)
8. M. Leitner, G. Vogl, Quasi-elastic scattering under short-range order: the linear regime and beyond. *J. Phys. Condens. Matter* **23**, 254206 (2011)
9. O.G. Randl, B. Sepiol, G. Vogl, R. Feldwisch, K. Schroeder, Quasielastic Mössbauer spectroscopy and quasielastic neutron scattering from non-Bravais lattices with differently occupied sublattices. *Phys. Rev. B* **49**, 8768 (1994)
10. J.M. Rowe, K. Sköld, H.E. Flotow, J.J. Rush, Quasielastic neutron scattering by hydrogen in the  $\alpha$  and  $\beta$  phases of vanadium hydride. *J. Phys. Chem. Solids* **32**, 41 (1971)
11. S.K. Sinha, D.K. Ross, Self-consistent density response function method for dynamics of light interstitials in crystals. *Physica B* **149**, 51 (1988)
12. L. van Hove, Correlations in space and time and born approximation scattering in systems of interacting particles. *Phys. Rev.* **95**, 249 (1954)
13. G.H. Vineyard, Frequency factors and isotope effects in solid state rate processes. *J. Phys. Chem. Solids* **3**, 121 (1957)

Studying Atomic Dynamics with Coherent X-rays

Leitner, M.

2012, X, 98 p., Hardcover

ISBN: 978-3-642-24120-8