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A lattice gas model for the Zener relaxation

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Abstract. The Zener relaxation is an anelastic relaxation process in disordered crystals due to stress-induced changes of atomic order. We present a model calculation of this process for a simple cubic lattice gas which is non-interacting except for the exclusion of multiple occupancies. The relaxation results from the stress-induced formation and dissolution of bonds between (paired) lattice gas atoms on nearest-neighbour sites. Relaxation spectra are obtained for the compressibility $s_{11}+2s_{12}$ and the shear compliance $s_{11}-s_{12}$. The spectra are proportional to $c^2(1-c)^2$, where c is the occupation probability of a given site. The frequency dependence of the spectra is determined by the jump rate of the lattice gas atoms. Compared with a spectrum for a single relaxation time, the spectrum of $s_{11} - s_{12}$ is moderately broadened, whereas the spectrum of $s_{11} + 2s_{12}$ shows a sizable broadening. The present results are applicable to both interstitial and substitutional alloys.

1. Introduction

The Zener relaxation is an anelastic relaxation process in disordered crystals due to a stress-induced change of the atomic order. The atomic order changes by diffusive jumps of the atomic constituents so that the relaxation times are related to their jump rates. A detailed description of experimental data and the theoretical concepts of the Zener relaxation is given by Nowick and Berry [1].

An important characteristic of the Zener relaxation is that it occurs also in crystals whose symmetry makes all atomic positions equivalent with respect to an externally applied stress. It differs, in this respect, from the (conceptionally simpler) Snoek relaxation which results from a stress-induced population exchange between sites that respond differently to external stress [1, 2]. The occurrence of the Zener relaxation requires, accordingly, the existence of spatial atomic configurations of at least two (pairs) or more atoms which differ in their energy under stress. This fact makes a theoretical modelling of the Zener relaxation far more complex than that of the Snoek relaxation. The Zener relaxation exhibits further similarities to the relaxation processes in glasses or polymers [3]. However, the analogy is certainly not complete since at least the low-temperature anelastic properties of crystals exhibiting Zener relaxation differ from a standard glassy behaviour [4].

Interstitial alloys are a specific class of compounds, where Zener relaxation is observed. In such alloys, the host lattice atoms are immobile, at least at low temperatures, whereas the interstitial atoms can diffuse as a lattice gas. Since the (interstitial) sites of such a lattice gas are either populated by interstitial atoms (component 1) or by vacancies (component 2), Zener relaxation can take place precisely as in a two-component substitutional alloy. Metal–hydrogen systems are an interesting realization of such a lattice gas because of the high diffusivity of the hydrogen interstitials [5, 6], so the Zener relaxation in these systems was

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intensively investigated, for instance in Pd [7–12] and in Sc and Y [13–17]. It is worth mentioning that a pure Zener relaxation was studied in these cases since the symmetry of the interstitial sites of the hydrogen (octahedral sites in face-centred cubic (fcc) Pd and tetrahedral ones in hexagonal close-packed (hcp) Sc and Y) excludes the occurrence of a Snoek relaxation.

Because of the complex nature of the Zener relaxation, the presently existing theoretical models for this process [1, 2, 11, 12, 18–24] are still very crude and approximate. Even in the simplest case of dilute alloys, where the relaxation can be traced to pairs of the solute atoms [1, 2, 18], the relaxation kinetics has only been treated in a highly simplified manner. Experiments on Li pairs in Al [25] are an example of a Zener relaxation study on such a dilute alloy. The situation is much more complex in concentrated alloys where the atomic order is no longer describable in terms of isolated pairs of atoms of one of the alloy constituents. In this case, expressions for the relaxation strength were derived in model calculations [1, 2, 11, 12, 19, 20, 22–24] which considered, in most cases, the effects of a stress-induced change of short-range order parameters (a critical discussion of the merits and the problems of this concept is given in [22]). Further, a model calculation for the relaxation kinetics of the short-range order parameters was performed [21], yielding identical relaxation rates for all the order parameters considered. Therefore, this calculation cannot explain different relaxation rates for different elastic compliances such as, for instance, experimentally observed in the PdH_x system [11].

In this paper, we discuss the Zener relaxation of a concentrated lattice gas that is non-interacting except for the fact that a given site can be occupied only once. The lattice gas populates a simple cubic lattice, which excludes a Snoek relaxation [1, 2]. The anelastic relaxation results from the stress-induced formation and dissolution of bonds between two (paired) lattice gas atoms occupying nearest-neighbour sites. We derive, rigorously correct within the model assumptions, the anelastic relaxation spectra, using only three (adjustable) parameters (the jump rate of the atoms and two parameters describing the lattice strain from a bond). In agreement with previous models, a relaxation of both the compressibility $s_{11}+2s_{12}$ and the shear compliance $s_{11}-s_{12}$ is found, being proportional to $c^2(1-c^2)$ where c is the occupation probability of a given site; the shear compliance $s_{44}/2$ does not relax for symmetry reasons (s_{11}, s_{12} and s_{44} are elastic compliances in Voigt's notation [1, 2, 26, 27], and $s_{11}+2s_{12}$, $s_{11}-s_{12}$ and $s_{44}/2$ are named compressibility or shear compliances although these quantities are conventionally defined as $3(s_{11}+2s_{12})$, $2(s_{11}-s_{12})$ and s_{44}, respectively). The new results of the present calculations address the kinetics of the relaxation process, expressed by the frequency dependence of the relaxation spectra (or, alternatively, by the distribution function of the relaxation times). This kinetics is characterized by a relaxation spectrum of $s_{11}-s_{12}$ that is moderately broadened in comparison with a standard Debye relaxation (a single relaxation time) [1], and by a relaxation spectrum of $s_{11}+2s_{12}$ that is significantly broadened.

The basic assumptions of the present lattice gas model are simpler and the number of adjustable parameters (three) is smaller than in most previous Zener relaxation theories for concentrated alloys. The fact that a non-interacting lattice gas (non-interacting except for the exclusion of multiple occupancies) is considered means that possible energy differences between different atomic configurations are not taken into account. On the other hand, the theoretical concept by which the relaxation spectra are calculated for the present model differs radically from previous procedures. It is based on a straightforward application of the fluctuation–dissipation theorem to the strain fluctuations that are caused by the diffusing lattice gas atoms. With the help of this theoretical concept, the relaxation spectra are calculated rigorously correctly within the model assumptions, without any approximation.

In particular, the present calculations are the first ones that provide a treatment of the kinetics of the Zener relaxation that is inherently correct, which means that is free from approximations and simplifications.

2. The lattice gas model

We consider a concentrated lattice gas that is non-interacting except for the exclusion of multiple occupancies. The lattice is simple cubic with a lattice parameter a, extending over N lattice sites within a cube of volume V (a cube for reasons of simplicity). Later, we go to the limits $V \to \infty$ and $N \to \infty$, where $V/N = a^3$. The occupation probability of a given lattice site is c (the concentration of the lattice gas), so that the total number of lattice gas atoms is Nc. Each atom can jump with a jump rate Γ to any of its six nearest-neighbour lattice sites, if this site is not occupied (blocked) by another atom. Accordingly, the mean residence time of an atom is $\tau_{res}(c \to 0) = 1/(6\Gamma)$ in the limit $c \to 0$ where no blocking exists, whereas blocking effects make it larger than $\tau_{res}(c \to 0)$ with increasing c [28].

An important quantity is the number of bonds between two (paired) atoms occupying two nearest-neighbour sites (with a distance a). A bond exists if both sites are simultaneously occupied. Figure 1 shows a two-dimensional example for these bonds. There are bonds of types x, y and z, depending on the direction of the line between the two occupied sites. The total number of bonds of types x, y and z in V is Z_x, Z_y and Z_z, respectively. These numbers fluctuate in time around their expectation (or average) values $\langle Z_x \rangle$, $\langle Z_y \rangle$ and $\langle Z_z \rangle$, and the deviations from the expectation value are $\Delta Z_x = Z_x - \langle Z_x \rangle$, $\Delta Z_y = Z_y - \langle Z_y \rangle$ and $\Delta Z_z = Z_z - \langle Z_z \rangle$.

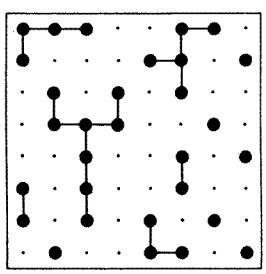

Figure 1. A two-dimensional example for the bonds between two nearest-neighbour lattice gas atoms. The large full circles and the small dots represent lattice gas atoms (or occupied lattice sites) and vacancies (unoccupied lattice sites), respectively. Each of the existing bonds is indicated by a line that connects two nearest-neighbour lattice gas atoms. According to the directions of the X and Y axes, the horizontal and the vertical lines represent bonds of types x and y, respectively.

Each bond is a point defect whose anelastic behaviour can be described by a $\boldsymbol{\lambda}$ tensor [1, 2]. The $\boldsymbol{\lambda}$ tensor $\lambda_{ij}^{(x)}$ of a bond of type x, for instance, can be written as

$$\lambda_{ij}^{(x)} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_2 \end{bmatrix}. \tag{1}$$

For symmetry reasons, there are only two independent parameters λ_1 and λ_2. The $\boldsymbol{\lambda}$ tensors $\lambda_{ij}^{(y)}$ and $\lambda_{ij}^{(z)}$ of the bonds of types y and z follow from (1) by cyclic permutation. With the

$\boldsymbol{\lambda}$ tensors, the lattice strain ϵ_{ij} caused by the bonds is given by [1, 2]

$$\epsilon_{ij} = (\Delta z_x/N)\lambda_{ij}^{(x)} + (\Delta Z_y/N)\lambda_{ij}^{(y)} + (\Delta Z_z/N)\lambda_{ij}^{(z)} \tag{2}$$

where the reference state of zero strain is a situation in which the bond numbers Z_x, Z_y and Z_z assume their expectation values.

The above definitions complete the description of our lattice gas model. However, one point remains to be mentioned. The sole fact of lattice strains such as those described by the $\boldsymbol{\lambda}$ tensors gives rise to an elastic interaction between the lattice gas atoms, in contrast to our assumption that these atoms are non-interacting (except for the absence of multiple occupancies) [1, 2, 26, 29]. In the case of the Snoek effect, where the same problem arises, Nowick and Heller [2] showed that the influence of the elastic interaction on the relaxation is insignificant as long as the relaxation strengths are small. The same conclusion holds for the present situation, so our later results are valid in cases where the relaxation strengths are small.

3. The fluctuations of orthogonal and normalized strains

3.1. The fluctuation–dissipation theorem

We apply the fluctuation–dissipation theorem [30] to orthogonal (symmetrized) and normalized strains and stresses [1, 2, 26]. For cubic symmetry, as for our lattice gas, the complex strain–stress relationship for a given pair of orthogonal and normalized strain $\tilde{\epsilon}$ and stress $\tilde{\sigma}$ is described by a single elastic compliance $\tilde{\sigma}(\omega)$, according to

$$\tilde{\epsilon}(\omega) = \tilde{s}(\omega)\tilde{\sigma}(\omega). \tag{3}$$

The complex compliance $\tilde{s}(\omega)$ has a real part $\tilde{s}'(\omega)$ and an imaginary part $\tilde{s}''(\omega)$. The latter is also called the relaxation spectrum of $\tilde{s}(\omega)$. The imaginary part $\tilde{s}''(\omega)$ is zero in the limit $\omega \to \infty$ and (in the present case) also for $\omega = 0$. This means $\tilde{s}(\omega) = \tilde{s}'(\omega)$ for $\omega = 0$ and $\omega \to \infty$. Because of the normalization, the free enthalpy (Gibbs' energy) per unit volume is, in the presence of a static stress $\tilde{\sigma}(\omega = 0)$, given by

$$g = \tfrac{1}{2}\tilde{s}(\omega = 0)\tilde{\sigma}^2(\omega = 0). \tag{4}$$

We consider next the correlation function $\langle\tilde{\epsilon}(t)\tilde{\epsilon}(t = 0)\rangle$ for the fluctuations of $\tilde{\epsilon}$ in V with time t. It is an even time function within classical statistics. The fluctuation–dissipation theorem (classical statistics) relates the imaginary part of the compliance to the correlation function of $\tilde{\epsilon}$ according to [30]

$$\tilde{s}''(\omega) = \frac{\omega V}{2k_B T}\int_{-\infty}^{\infty}\langle\tilde{\epsilon}(t)\tilde{\epsilon}(t = 0)\rangle\, \mathrm{e}^{\mathrm{i}\omega t}\, \mathrm{d}t. \tag{5}$$

The frequency variation of the real part of the compliance can be obtained from the Kramers–Kronig relations [30]. The total relaxation $\Delta\tilde{s} = \tilde{s}(\omega = 0) - \tilde{s}(\omega \to \infty) = \tilde{s}'(\omega = 0) - \tilde{s}'(\omega \to \infty)$ of the compliance $\tilde{s}(\omega)$, in particular, is given by [30]

$$\Delta\tilde{s} = \frac{V}{k_B T}\langle\tilde{\epsilon}^2(t)\rangle \tag{6}$$

where the correlation amplitude $\langle\tilde{\epsilon}^2(t)\rangle$ is independent of t.

The presence of V in (5) and (6) follows from the fact that (4) describes the free enthalpy per unit volume rather than in the volume V. It reflects also the fact that strain fluctuations, averaged over a volume, are smaller for larger volume. The volume V does not appear in the equations of [30] that correspond to (5) and (6). The reason is that the

quantities that correspond to $\tilde{\epsilon}$ and $\tilde{\sigma}$ in [30] are a true displacement and a true force, also in their dimension, rather than a strain and a stress. Appendix A demonstrates how V shows up in (5) and (6) if we transform strain and stress appropriately in displacement and force.

3.2. The orthogonal and normalized strains and their correlation functions

Since strain and stress have six independent tensor components each, we can define six pairs of orthogonal and normalized strains $\tilde{\epsilon}^{(\nu)}$ and stresses $\tilde{\sigma}^{(\nu)}$ [1, 2, 26]. For a cubic system, the strain–stress relationship for a given ν is expressed by a single elastic compliance $\tilde{s}^{(\nu)}$, and there exist only three different compliances $\tilde{s}^{(1)} = s_{11} + 2s_{12}$, $\tilde{s}^{(2)} = \tilde{s}^{(3)} = s_{12} - s_{12}$ and $\tilde{s}^{(4)} = \tilde{s}^{(5)} = \tilde{s}^{(6)} = s_{44}/2$. Further, since $s_{44}/2$ does not relax in the present situation for symmetry reasons, it suffices to consider the first two of the six pairs of orthogonal and normalized strains and stresses, associated with the compressibility $s_{11} + 2s_{12}$ and the shear compliance $s_{11} - s_{12}$.

We discuss $\tilde{s}^{(1)} = s_{11} + 2s_{12}$ first. In this case, the associated orthogonal and normalized strain and stress tensors are, in tensor notation, defined as [26]

$$\epsilon_{ij}^{(1)} = \frac{1}{\sqrt{3}} \begin{bmatrix} \tilde{\epsilon}^{(1)} & 0 & 0 \\ 0 & \tilde{\epsilon}^{(1)} & 0 \\ 0 & 0 & \tilde{\epsilon}^{(1)} \end{bmatrix} \qquad \sigma_{ij}^{(1)} = \frac{1}{\sqrt{3}} \begin{bmatrix} \tilde{\sigma}^{(1)} & 0 & 0 \\ 0 & \tilde{\sigma}^{(1)} & 0 \\ 0 & 0 & \tilde{\sigma}^{(1)} \end{bmatrix}. \tag{7}$$

According to these definitions, the strain–stress relation between $\tilde{\epsilon}^{(1)}$ and $\tilde{\sigma}^{(1)}$ is indeed described by $\tilde{s}^{(1)} = s_{11} + 2s_{12}$, and the energy relation (4) holds.

The relaxation behaviour of $\tilde{s}^{(1)}$ depends on the fraction of the strain ϵ_{ij} from the bonds in (2) that is represented by $\tilde{\epsilon}^{(1)}$ (the projection of ϵ_{ij} on $\tilde{\epsilon}^{(1)}$). From the trace of ϵ_{ij} in (2) and of $\epsilon_{ij}^{(1)}$ in (7), for instance, we find

$$\tilde{\epsilon}^{(1)} = (1/\sqrt{3})(\lambda_1 + 2\lambda_2)\{\Delta Z_x/N + \Delta Z_y/N + \Delta Z_z/N\}. \tag{8}$$

This result allows the calculation of the correlation function $\langle \tilde{\epsilon}^{(1)}(t)\tilde{\epsilon}^{(1)}(t=0)\rangle$ from the correlation functions of the time-dependent quantities $\Delta Z_x(t)$, $\Delta Z_y(t)$ and $\Delta Z_z(t)$. With the help of (8), $\langle \tilde{\epsilon}^{(1)}(t)\tilde{\epsilon}^{(1)}(t=0)\rangle$ can be written as

$$\begin{aligned}\langle \tilde{\epsilon}^{(1)}(t)\tilde{\epsilon}^{(1)}(t=0)\rangle = {} & \frac{(\lambda_1 + 2\lambda_2)^2}{3N^2}\langle\{\Delta Z_x(t) + \Delta Z_y(t) + \Delta Z_z(t)\}\{\Delta Z_x(t=0) \\ & + \Delta Z_y(t=0) + \Delta Z_z(t=0)\}\rangle.\end{aligned} \tag{9}$$

Due to the time-inversion symmetry of correlation functions and since, for instance, $\langle \Delta Z_x(t)\Delta Z_x(t=0)\rangle = \langle \Delta Z_y(t)\Delta Z_y(t=0)\rangle$ and $\langle \Delta Z_x(t)\Delta Z_y(t=0)\rangle = \langle \Delta Z_x(t)\Delta Z_z(t=0)\rangle$ hold for symmetry reasons, we can write

$$\begin{aligned}\langle \tilde{\epsilon}^{(1)}(t)\tilde{\epsilon}^{(1)}(t=0)\rangle = {} & \frac{(\lambda_1 + 2\lambda_2)^2}{N^2}\{\langle \Delta Z_x(t)\Delta Z_x(t=0)\rangle \\ & + 2\langle \Delta Z_x(t)\Delta Z_y(t=0)\rangle\}.\end{aligned} \tag{10}$$

From this equation and from (5) and (6), the relaxation of the compressibility can be determined from $\langle \Delta Z_x(t)\Delta Z_x(t=0)\rangle$ and $\langle \Delta Z_x(t)\Delta Z_y(t=0)\rangle$.

For the shear compliance $\tilde{s}^{(2)} = s_{12} - s_{12}$, the associated orthogonal and normalized stresses and strains are, in tensor notation, given by [26]

$$\epsilon_{ij}^{(2)} = \frac{1}{\sqrt{2}} \begin{bmatrix} \tilde{\epsilon}^{(2)} & 0 & 0 \\ 0 & -\tilde{\epsilon}^{(2)} & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad \sigma_{ij}^{(2)} = \frac{1}{\sqrt{2}} \begin{bmatrix} \tilde{\sigma}^{(2)} & 0 & 0 \\ 0 & -\tilde{\sigma}^{(2)} & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{11}$$

The strain–stress relationship between $\tilde{\epsilon}^{(2)}$ and $\tilde{\sigma}^{(2)}$ is again described by the compliance $\tilde{s}^{(2)}$ and the energy relation (4) holds. Further, it is found from (2) that the fraction of the strain ϵ_{ij} from the bonds that is represented by $\tilde{\epsilon}^{(2)}$ is given by

$$\tilde{\epsilon}^{(2)} = (1/\sqrt{2})(\lambda_1 - \lambda_2)\{\Delta Z_x/N - \Delta Z_y/N\}. \tag{12}$$

This follows, for instance, from the difference $\epsilon_{11} - \epsilon_{22}$ of the two components ϵ_{11} and ϵ_{22} of the strain tensor in (2). According to (12), the correlation function $\langle\tilde{\epsilon}^{(2)}(t)\tilde{\epsilon}^{(2)}(t=0)\rangle$ can be written as

$$\langle\tilde{\epsilon}^{(2)}(t)\tilde{\epsilon}^{(2)}(t=0)\rangle = \frac{(\lambda_1-\lambda_2)^2}{N^2}\{\langle\Delta Z_x(t)\Delta Z_x(t=0)\rangle - \langle\Delta Z_x(t)\Delta Z_y(t=0)\rangle\}. \tag{13}$$

In the subsequent chapters, we calculate $\langle\Delta Z_x(t)\Delta Z_x(t=0)\rangle$ and $\langle\Delta Z_x(t)\Delta Z_y(t=0)\rangle$ to determine the relaxation of $s_{11} + 2s_{12}$ and $s_{11} - s_{12}$. Further, to demonstrate how the formalism above works in the case of a well known problem, we derive in appendix B the total relaxation of $s_{11} - s_{12}$ in the case of the Snoek relaxation of octahedral interstitial atoms in bcc metals [1, 2].

4. The correlation functions of the numbers of bonds

4.1. Occupation numbers and their Fourier representation

We define, for each lattice site at position $\boldsymbol{R}$, a time-dependent occupation number $c(\boldsymbol{R}, t)$ that is one or zero depending on whether the site is occupied or not. The expectation value of $c(\boldsymbol{R}, t)$ is c, for all $\boldsymbol{R}$ and t, and the deviation of $c(\boldsymbol{R}, t)$ from c is $\Delta c(\boldsymbol{R}, t) = c(\boldsymbol{R}, t) - c$. In our calculations, we conserve the total number Nc of lattice gas atoms. Accordingly, the summations $\sum_{\boldsymbol{R}} c(\boldsymbol{R}, t)$ and $\sum_{\boldsymbol{R}} \Delta c(\boldsymbol{R}, t)$ over the N lattice sites yield Nc and zero, respectively.

Following Krivoglaz [31], we consider the Fourier representation of $\Delta c(\boldsymbol{R}, t)$,

$$\Delta c(\boldsymbol{k}, t) = \frac{1}{N}\sum_{\boldsymbol{R}} \Delta c(\boldsymbol{R}, t)\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \qquad \text{and} \qquad \Delta c(\boldsymbol{R}, t) = \sum_{\boldsymbol{k}} \Delta c(\boldsymbol{k}, t)\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}. \tag{14}$$

This transformation is possible since we discuss the limits $V \to \infty$ and $N \to \infty$ (with $V/N = a^3$). Later, the second summation is replaced by an integration over the first Brillouin zone, which corresponds to the transition

$$\sum_{\boldsymbol{k}} \to N\left(\frac{a}{2\pi}\right)^3 \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \mathrm{d}^3\boldsymbol{k}. \tag{15}$$

According to (14), $\Delta c(-\boldsymbol{k}, t)$ is the conjugate complex of $\Delta c(\boldsymbol{k}, t)$, and the relations $\sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} = N\delta_{\boldsymbol{k},0}$ and $\sum_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} = N\delta_{\boldsymbol{R},0}$ hold ($\delta_{\boldsymbol{k},0}$ and $\delta_{\boldsymbol{R},0}$ are one or zero, depending on whether $\boldsymbol{k}$ or $\boldsymbol{R}$ are zero or not). Further, the constraint of a fixed number of lattice gas atoms, expressed by the relation $\sum_{\boldsymbol{R}} \Delta c(\boldsymbol{R}, t) = 0$, leads to $\Delta c(\boldsymbol{k} = 0, t) = 0$.

A final quantity of interest is the correlation amplitude $\langle\Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t)\rangle$, which will be written $\langle\Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle$ since it is independent of t. According to Krivoglaz [31], this quantity is given by

$$\langle\Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle = c(1-c)/N. \tag{16}$$

We must consider here that (16) was derived for a case in which fluctuations of the total number of lattice gas atoms were allowed, whereas the present calculations keep the number of atoms fixed. An immediate consequence of this constraint is that $\langle\Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle$ is

zero for $\boldsymbol{k} = \mathbf{0}$. However, our present calculations require this quantity only for $\boldsymbol{k} \neq \mathbf{0}$, for which the difference between a fluctuating and a fixed number of atoms is insignificant for $N \to \infty$. This is demonstrated in appendix C. For this reason, we shall use, for $\boldsymbol{k} \neq \mathbf{0}$, the result of (16) in our calculations.

It is preferable to conserve the number of atoms in the present calculations since a fluctuation of this number means the possibility of an exchange of atoms between a sample and its surroundings, due to in- or out-diffusion. This causes an (additional) anelastic relaxation with relaxation times that correspond to the times required for the in or out diffusion to take place. Such a relaxation (a type of Gorsky relaxation [1, 5]) differs from the Zener relaxation and is not considered here.

4.2. The diffusion of the lattice gas atoms

The diffusion of the lattice gas atoms is described by a rate equation for the occupation number $c(\boldsymbol{R}, t)$ of a site at $\boldsymbol{R}$ due to diffusive jumps between this site and the six nearest-neighbour sites at $\boldsymbol{R}+\boldsymbol{a}_x$, $\boldsymbol{R}-\boldsymbol{a}_x$, $\boldsymbol{R}+\boldsymbol{a}_y$, $\boldsymbol{R}-\boldsymbol{a}_y$, $\boldsymbol{R}+\boldsymbol{a}_z$ and $\boldsymbol{R}-\boldsymbol{a}_z$, where $\boldsymbol{a}_x$, $\boldsymbol{a}_y$ and $\boldsymbol{a}_z$ are vectors of length a in the direction of the X-, Y- and Z-axis, respectively. With the jump rate Γ to a given unoccupied nearest-neighbour site, the rate equation can be written as

$$\begin{aligned}\langle \mathring{c}(\boldsymbol{R}, t)\rangle_D = \Gamma\{&-c(\boldsymbol{R}, t)(1 - c(\boldsymbol{R} + \boldsymbol{a}_x, t)) + c(\boldsymbol{R} + \boldsymbol{a}_x, t)(1 - c(\boldsymbol{R}, t)) \\ &+\text{the terms for the sites at } \boldsymbol{R} - \boldsymbol{a}_x, \boldsymbol{R} + \boldsymbol{a}_y, \boldsymbol{R} - \boldsymbol{a}_y, \boldsymbol{R} + \boldsymbol{a}_z \text{ and} \boldsymbol{R} - \boldsymbol{a}_z\}.\end{aligned} \tag{17}$$

The first two (explicitly stated) terms in the curly brackets of the right-hand side of (17) account for the exchange of atoms between the sites at $\boldsymbol{R}$ and $\boldsymbol{R} + \boldsymbol{a}_x$. The first term describes the jumps from $\boldsymbol{R}$ to $\boldsymbol{R} + \boldsymbol{a}_x$, which can occur with a jump rate Γ if both the site at $\boldsymbol{R}$ is occupied (factor $c(\boldsymbol{R}, t)$) and the site at $\boldsymbol{R} + \boldsymbol{a}_x$ is unoccupied (factor $1 - c(\boldsymbol{R} + \boldsymbol{a}_x, t)$). The second term stands for the corresponding jumps from $\boldsymbol{R} + \boldsymbol{a}_x$ to $\boldsymbol{R}$. Accordingly, the rate equation (17) accounts correctly for all blocking effects. It is further seen that the quadratic terms in the curly brackets of (17) cancel out. With the identity $\Delta\, \mathring{c}(\boldsymbol{R}, t) = \mathring{c}(\boldsymbol{R}, t)$, we can rewrite (17) as

$$\begin{aligned}\langle \Delta\, \mathring{c}(\boldsymbol{R}, t)\rangle_D = \Gamma\{&-6\Delta c(\boldsymbol{R}, t) + \Delta c(\boldsymbol{R} + \boldsymbol{a}_x, t) + \Delta c(\boldsymbol{R} - \boldsymbol{a}_x, t) \\ &+\text{terms with } \boldsymbol{a}_y \text{ and } \boldsymbol{a}_z\}.\end{aligned} \tag{18}$$

The left-hand sides of (17) and (18) express an expectation value for $\mathring{c}(\boldsymbol{R}, t)$ (or $\Delta\, \mathring{c}(\boldsymbol{R}, t)$) due to the diffusion of the lattice gas atoms, valid under the condition that the actual values of the occupation numbers, at time t, are $c(\boldsymbol{R}, t)$, $c(\boldsymbol{R} + \boldsymbol{a}_x, t)$ etc. This fact is indicated by the brackets with the subscript D.

Passing to the Fourier transforms $\Delta c(\boldsymbol{k}, t)$, (18) is now given by

$$\langle \Delta\, \mathring{c}(\boldsymbol{k}, t)\rangle_D = \Gamma \Delta c(\boldsymbol{k}, t)\{-6 + \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_x} + \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_x} + \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_y} + \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_y} + \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_z} + \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_z}\} \tag{19}$$

where the terms $\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_x}$, $\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_x}$ etc stand for the terms $\Delta c(\boldsymbol{R} + \boldsymbol{a}_x, t)$, $\Delta c(\boldsymbol{R} - \boldsymbol{a}_x, t)$ etc in (18). Considering, for instance, the identity $4\sin^2(\boldsymbol{k} \cdot \boldsymbol{a}_x/2) = 2 - \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_x} - \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_x}$, and using $k_x a$, $k_y a$ and $k_z a$ rather than $\boldsymbol{k} \cdot \boldsymbol{a}_x$, $\boldsymbol{k} \cdot \boldsymbol{a}_y$ and $\boldsymbol{k} \cdot \boldsymbol{a}_z$, we can write (19) as

$$\langle \Delta\, \mathring{c}(\boldsymbol{k}, t)\rangle_D = -[p(\boldsymbol{k})/2]\Delta c(\boldsymbol{k}, t) \tag{20}$$

where $p(\boldsymbol{k})$ is defined by

$$p(\boldsymbol{k}) = 8\Gamma\{\sin^2(k_x a/2) + \sin^2(k_y a/2) + \sin^2(k_z a/2)\}. \tag{21}$$

That $p(\boldsymbol{k})$ is independent of c expresses the fact that the decay rate of density fluctuations in a concentrated lattice gas as defined in section 2 does not depend on concentration [28, 32].

The integration of (20) yields a diffusion-induced exponential decay of $\Delta c(\boldsymbol{k}, t)$. However, rather than $\Delta c(\boldsymbol{k}, t)$ itself we need to discuss the influence of the diffusion on the product $\Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t)$ between $\Delta c(\boldsymbol{k}, t)$ and its conjugate complex. Considering that $(\mathrm{d}/\mathrm{d}t)(\Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t)) = \Delta \overset{\circ}{c}(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t) + \Delta c(\boldsymbol{k}, t)\Delta \overset{\circ}{c}(-\boldsymbol{k}, t)$, that $p(\boldsymbol{k}) = p(-\boldsymbol{k})$ and that $\langle \Delta \overset{\circ}{c}(\boldsymbol{k}, t)\rangle_D$ and $\langle \Delta \overset{\circ}{c}(-\boldsymbol{k}, t)\rangle_D$ are given by (20) or its conjugate complex, we find

$$\langle (\mathrm{d}/\mathrm{d}t)(\Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t))\rangle_D = -p(\boldsymbol{k})\, \Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t). \tag{22}$$

From (22), we can calculate, for $t \geqslant 0$, the expectation value $\langle(\Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t))\rangle_D$ due to the diffusion process, found for a given initial $\Delta c(\boldsymbol{k}, t = 0)\Delta c(-\boldsymbol{k}, t = 0)$. What is additionally required is the final value to which $\langle(\Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t))\rangle_D$ decays in the limit $t \to \infty$. This final value is the expectation value $\langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle$, so an integration of (22) yields

$$\begin{aligned}\langle(\Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t))\rangle_D = \langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle + \{\Delta c(\boldsymbol{k}, t = 0)\Delta c(-\boldsymbol{k}, t = 0)\\ -\langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle\}\, \mathrm{e}^{-p(\boldsymbol{k})t}.\end{aligned} \tag{23}$$

This equation shows an exponential decay with a time constant $1/p(\boldsymbol{k})$.

4.3. The numbers of bonds and their correlation functions

In this chapter, we calculate the correlation functions $\langle \Delta Z_x(t)\Delta Z_x(t{=}0)\rangle$ and $\langle \Delta Z_x(t)\Delta Z_y(t = 0)\rangle$. Consider the product $c(\boldsymbol{R}, t)c(\boldsymbol{R}+\boldsymbol{a}_x, t)$, which is unity if the bond (of type x) between the sites at $\boldsymbol{R}$ and $\boldsymbol{R} + \boldsymbol{a}_x$ exists and is zero otherwise. Accordingly, the number $Z_x(t)$ of bonds of type x at time t is given by

$$\begin{aligned}Z_x(t) &= \sum_{\boldsymbol{R}} c(\boldsymbol{R}, t)c(\boldsymbol{R} + \boldsymbol{a}_x, t) = \sum_{\boldsymbol{R}} \{\Delta c(\boldsymbol{R}, t) + c\}\{\Delta c(\boldsymbol{R} + \boldsymbol{a}_x, t) + c\}\\ &= \sum_{\boldsymbol{R}} \Delta c(\boldsymbol{R}, t)\, \Delta c(\boldsymbol{R} + \boldsymbol{a}_x, t) + Nc^2.\end{aligned} \tag{24}$$

The second expression holds because $\sum_{\boldsymbol{R}} \Delta c(\boldsymbol{R}, t) = \sum_{\boldsymbol{R}} \Delta c(\boldsymbol{R} + \boldsymbol{a}_x, t) = 0$. Passing to the Fourier transforms $\Delta c(\boldsymbol{k}, t)$, we can rewrite (24) as

$$Z_x(t) = N \sum_{\boldsymbol{k}\neq 0} \Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t)\, \mathrm{e}^{-k_x a} + Nc^2. \tag{25}$$

The term for $\boldsymbol{k} = \boldsymbol{0}$ is omitted in the summation since $\Delta c(\boldsymbol{k} = \boldsymbol{0}, t) = 0$, and symmetry allows replacing $\mathrm{e}^{-k_x a}$ by $\cos(k_x a)$ in the following equations. According to (25), the deviation $\Delta Z_x(t) = Z_x(t) - \langle Z_x(t)\rangle$ of $Z_x(t)$ from its expectation value is given by

$$\Delta Z_x(t) = N \sum_{\boldsymbol{k}\neq \boldsymbol{0}} \{\Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t) - \langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle\} \cos(k_x a). \tag{26}$$

In the corresponding expression for $\Delta Z_y(t)$, $\cos(k_x a)$ is replaced by $\cos(k_y a)$.

We consider next the correlation functions, and calculate $\langle \Delta Z_x(t)\Delta Z_x(t = 0)\rangle$ first. Replacing $\Delta c(\boldsymbol{k}, t)\Delta c(-\boldsymbol{k}, t)$ in (26) by its expectation value due to diffusion as given in (23), and averaging over all initial $\Delta c(\boldsymbol{k}, t = 0)\Delta c(-\boldsymbol{k}, t = 0)$, we find

$$\begin{aligned}\langle \Delta Z_x(t)\Delta Z_x(t = 0)\rangle = N^2 \Bigg\langle \sum_{\boldsymbol{k}\neq \boldsymbol{0}} \{\Delta c(\boldsymbol{k}, t = 0)\Delta c(-\boldsymbol{k}, t = 0) - \langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle\}\\ \times \cos(k_x a)\, \mathrm{e}^{-p(\boldsymbol{k})|t|} \sum_{\boldsymbol{k}'\neq \boldsymbol{0}} \{\Delta c(\boldsymbol{k}', t = 0)\Delta c(-\boldsymbol{k}', t = 0)\end{aligned}$$

$$-\langle\Delta c(\boldsymbol{k}')\Delta c(-\boldsymbol{k}')\rangle\}\cos(k'_x a)\Big\rangle \tag{27}$$

Since the correlation function is an even time function, we accounted in (27) also for negative times by writing the absolute value of t in the exponential function. Omitting the time variable in the correlation amplitudes (but not in the correlation function), and defining $\boldsymbol{k}_1 \neq \boldsymbol{0}$, plus $\boldsymbol{k}_2 \neq \boldsymbol{0}$ and $\boldsymbol{k}_2 \neq \boldsymbol{k}_1$ later, (27) yields

$$\langle\Delta Z_x(t)\Delta Z_x(t=0)\rangle = N^2\sum_{\boldsymbol{k}\neq\boldsymbol{0}}\sum_{\boldsymbol{k}'\neq\boldsymbol{0}}\{\langle\Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\Delta c(\boldsymbol{k}')\Delta c(-\boldsymbol{k}')\rangle - \langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\rangle^2\}\cos(k_x a)\cos(k'_x a)\,\mathrm{e}^{-p(\boldsymbol{k})|t|}. \tag{28}$$

To proceed further, we use the identity (for $\boldsymbol{k} \neq \boldsymbol{0}$ and $\boldsymbol{k}' \neq \boldsymbol{0}$)

$$\langle\Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\Delta c(\boldsymbol{k}')\Delta c(-\boldsymbol{k}')\rangle = \langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\Delta c(\boldsymbol{k}_2)\Delta c(-\boldsymbol{k}_2)\rangle + \{\langle(\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1))^2\rangle - \langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\Delta c(\boldsymbol{k}_2)\Delta c(-\boldsymbol{k}_2)\rangle\}\delta_{\boldsymbol{k},\pm\boldsymbol{k}'} \tag{29}$$

with which the right-hand side of (28) can be split up into two terms

$$\langle\Delta Z_x(t)\Delta Z_x(t=0)\rangle = 2N^2\sum_{\boldsymbol{k}\neq\boldsymbol{0}}\{\langle(\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1))^2\rangle - \langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\Delta c(\boldsymbol{k}_2)\times\Delta c(-\boldsymbol{k}_2)\rangle\}\cos^2(k_x a)\,\mathrm{e}^{-p(\boldsymbol{k})|t|} + N^2\sum_{\boldsymbol{k}\neq\boldsymbol{0}}\sum_{\boldsymbol{k}'\neq\boldsymbol{0}}\{\langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\Delta c(\boldsymbol{k}_2)\times\Delta c(-\boldsymbol{k}_2)\rangle - \langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\rangle^2\}\cos(k_x a)\cos(k'_x a)\,\mathrm{e}^{-p(\boldsymbol{k})|t|}. \tag{30}$$

The first sum on the right-hand side extends solely over $\boldsymbol{k}$ (its factor of two reflects the fact that $\delta_{\boldsymbol{k}\neq\boldsymbol{k}'}$ in (29) applies for both $\boldsymbol{k} = \boldsymbol{k}'$ and $\boldsymbol{k} = -\boldsymbol{k}'$). Finally, we consider that the only term in the second sum that depends on $\boldsymbol{k}'$ is $\cos(k'_x a)$, and that a summation over $\boldsymbol{k}'$ which includes $\boldsymbol{k}' = \boldsymbol{0}$ would yield zero because of this term. By adding and subtracting such a term for $\boldsymbol{k}' = \boldsymbol{0}$, we can write (30) as

$$\langle\Delta Z_x(t)\Delta Z_x(t=0)\rangle = 2N^2\sum_{\boldsymbol{k}\neq\boldsymbol{0}}\{\langle(\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1))^2\rangle - \langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\Delta c(\boldsymbol{k}_2)\times\Delta c(-\boldsymbol{k}_2)\rangle\}\cos^2(k_x a)\,\mathrm{e}^{-p(\boldsymbol{k})|t|} - N^2\sum_{\boldsymbol{k}\neq\boldsymbol{0}}\{\langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\times\Delta c(\boldsymbol{k}_2)\Delta c(-\boldsymbol{k}_2)\rangle - \langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\rangle^2\}\cos(k_x a)\,\mathrm{e}^{-p(\boldsymbol{k})|t|} \tag{31}$$

where both integrals on the right-hand side extend only over $\boldsymbol{k}$.

We consider now the limit $N \to \infty$. Appendix C shows that, in this limit, $\langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\Delta c(\boldsymbol{k}_2)\Delta c(-\boldsymbol{k}_2)\rangle$ and $\langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\rangle^2$ differ insignificantly, so that the second sum of the right-hand side of (31) can be neglected (the fluctuations of $\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)$ are uncorrelated for different $\boldsymbol{k}_1$). It shows also that the expression $\langle(\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1))^2\rangle - \langle\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\Delta c(\boldsymbol{k}_2)\Delta c(-\boldsymbol{k}_2)\rangle$ in the first sum is given by $\langle\Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle^2$, which is $c^2(1-c)^2/N^2$ according to (16). Using these results, and passing from a sum to an integral over the first Brillouin zone (15), we can write (31) as

$$\langle\Delta Z_x(t)\Delta Z_x(t=0)\rangle = 2Nc^2(1-c)^2\left(\frac{a}{2\pi}\right)^3 \times\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\cos^2(k_x a)\,\mathrm{e}^{-p(\boldsymbol{k})|t|}\,\mathrm{d}^3\boldsymbol{k} \tag{32}$$

where the exclusion of the point at $\boldsymbol{k} = \boldsymbol{0}$ is disregarded because of the limit $N \to \infty$. Specifically for $t = 0$ (where $\exp(-p(\boldsymbol{k})|t|) = 1$), the integral of $\cos^2(k_x a)$ over the first Brillouin zone yields $\frac{1}{2}(2\pi/a)^3$, so that fluctuation amplitude $\langle\Delta Z_x(t=0)\Delta Z_x(t=0)\rangle = \langle\Delta Z_x^2\rangle$ is given by the simple expression

$$\langle\Delta Z_x^2\rangle = Nc^2(1-c)^2. \tag{33}$$

The calculation of $\langle \Delta Z_x(t)\Delta Z_y(t=0)\rangle$ is performed in the same way as that leading to (32), yielding

$$\langle \Delta Z_x(t)\Delta Z_y(t=0)\rangle = 2Nc^2(1-c)^2\left(\frac{a}{2\pi}\right)^3 \times \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \cos(k_x a)\cos(k_y a)\,\mathrm{e}^{-p(\boldsymbol{k})|t|}\,\mathrm{d}^3\boldsymbol{k}. \tag{34}$$

Finally, for $t = 0$, the fluctuation amplitude $\langle \Delta Z_x \Delta Z_y\rangle$ is given by

$$\langle \Delta Z_x \Delta Z_y\rangle = 0 \tag{35}$$

because of either of the terms $\cos(k_y a)$ or $\cos(k_y a)$ under the integral in (34). This means that there is no correlation in the numbers of bonds of types x and y at the same time, whereas a correlation exists at different times since, in this case, $\exp(-p(\boldsymbol{k})|t|)$ varies with $\boldsymbol{k}$ so the integral over the first Brillouin zone differs from zero.

5. The relaxation spectra and their discussion

The previous sections provide all the equations required for the calculation of the relaxation of the compressibility $\tilde{s}^{(1)} = s_{11} + 2s_{12}$ and of the shear compliance $\tilde{s}^{(2)} = s_{11} - s_{12}$. We discuss the compressibility first. According to (6), (10), (33) and (35), the total relaxation $\Delta(s_{12} + 2s_{12})$ of the compressibility is given by

$$\Delta(s_{12} + 2s_{12}) = (a^3/k_B T)c^2(1-c)^2(\lambda_1 + 2\lambda_2)^2 \tag{36}$$

where $a^3 = V/N$. The relaxation spectrum of the compressibility, i.e. its imaginary part $(s_{11} + 2s_{12})''$, is obtained from (5), (10), (32) and (34), where the Fourier transformation (5) of the exponential decay processes in the correlation functions of (32) and (34) yields Lorentzian lines. Using the total relaxation of (36), the relaxation spectrum of the compressibility can be written as

$$(s_{11} + 2s_{12})'' = \Delta(s_{12} + 2s_{12})\left(\frac{a}{2\pi}\right)^3 \times \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{2\omega p(\boldsymbol{k})}{\omega^2 + p^2(\boldsymbol{k})}\{\cos^2(k_x a) + 2\cos(k_x a)\cos(k_y a)\}\,\mathrm{d}^3\boldsymbol{k}. \tag{37}$$

For the shear compliance, the total relaxation $\Delta(s_{11} - s_{12})$ follows from (6), (13), (33) and (35). The result for this quantity is

$$\Delta(s_{12} - s_{12}) = (a^3/k_B T)c^2(1-c)^2(\lambda_1 - \lambda_2)^2. \tag{38}$$

From (5), (13), (32) and (34), the relaxation spectrum is, similarly to the above, obtained as

$$(s_{11} - s_{12})'' = \Delta(s_{12} - s_{12})\left(\frac{a}{2\pi}\right)^3 \times \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{2\omega p(\boldsymbol{k})}{\omega^2 + p^2(\boldsymbol{k})}\{\cos^2(k_x a) - \cos(k_x a)\cos(k_y a)\}\,\mathrm{d}^3\boldsymbol{k}. \tag{39}$$

The four equations (36)–(39) are our central result. In agreement with previous calculations [1, 2], they yield a relaxation of both $s_{11} + 2s_{12}$ and $s_{11} - s_{12}$, and they predict that the relaxation spectra are proportional to $c^2(1-c)^2$.

The derivation of the relaxation spectra is rigorously correct within our model assumptions. According to the definition of $p(\boldsymbol{k})$ in (21), the spectra depend only on three (adjustable) parameters, the jump rate Γ and the two components λ_1 and λ_2 of the $\boldsymbol{\lambda}$ tensor,

considering temperature and lattice parameter as given. The jump rate is subsequently expressed by the mean residence time $\tau_{res}(c \to 0) = 1/(6\Gamma)$ of the lattice gas atoms in the limit $c \to 0$ (see section 2).

The integrals in the relaxation spectra of (37) and (39) can only be evaluated numerically. To demonstrate their frequency dependence, we present in figure 2 the two relaxation spectra, normalized to the total relaxation, in a plot versus $\log(\omega\tau_{res}(c \to 0))$, together with a Debye peak [1] with a relaxation time $\tau_{res}(c \to 0)$. For a single relaxation time, normalized spectra have the shape of a Debye peak. The relaxation spectrum of the shear compliance is moderately broadened in comparison with a Debye peak, indicating a small distribution width of its relaxation times. The spectrum of the compressibility exhibits a sizable broadening so, in this case, widely different relaxation times contribute (in fact, the distribution of the relaxation times can directly be obtained from the correlation functions in (32) and (34)). Further, the maxima of the peaks for the compressibility and the shear compliance are at $\omega\tau_{res}(c \to 0) = 2.01$ and $\omega\tau_{res}(c \to 0) = 1.94$, respectively.

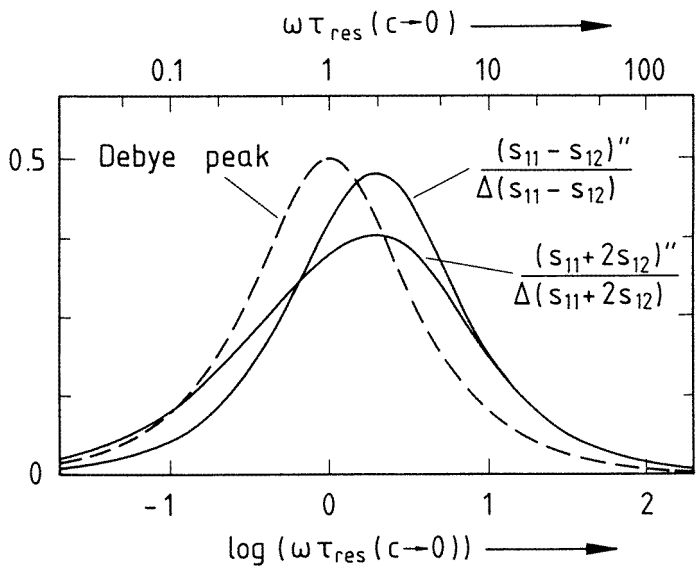

Figure 2. The normalized relaxation spectra (solid lines) $(s_{11} + 2s_{12})''/\Delta(s_{11} + 2s_{12})$ and $(s_{11} - s_{12})''/\Delta(s_{11} - s_{12})$ of the compressibility $s_{11} + 2s_{12}$ and the shear compliance $s_{11} - s_{12}$, respectively, in a plot versus $\log(\omega\tau_{res}(c \to 0))$. The spectra are normalized to their respective total relaxation strength. The broken line shows a Debye peak with a relaxation time $\tau_{res}(c \to 0)$.

The spectra exhibit a distribution of relaxation times, but these distributions are determined solely by the mean residence time $\tau_{res}(c \to 0)$. An immediate application follows if $\tau_{res}(c \to 0)$ exhibits an exponential temperature behaviour. In this case, the activation energy is reliably determined from a temperature shift of the peak maximum, although this is in general not possible for a distribution in the relaxation times (in this case, a further requirement is a common activation energy for all the relaxation times) [1]. The fact that the peak shift yields the true activation energy holds also for the generally expected situation that both the compressibility and the shear compliance $s_{11} - s_{12}$ contribute to the anelastic relaxation since the ratio between the total relaxations of the compressibility and the shear compliance is temperature independent.

The present lattice gas model holds for a simple cubic lattice and considers only bonds between nearest-neighbour sites. This is, in fact, the simplest version of such a model. There is no principal difficulty in adjusting it to other lattices, and to account additionally for bonds between more distant sites. In this case, a relaxation of the shear compliance $s_{44}/2$ will also be found. Finally, we recall the discussion in section 1, pointing out that the present results describe the Zener relaxation in both interstitial and substitutional alloys, in spite of the fact that a lattice gas model might primarily suggest an application to interstitial atoms.

6. Conclusion

We have discussed the anelastic Zener relaxation in a concentrated lattice gas which is non-interacting except for the exclusion of multiple occupancies. The relaxation results from the stress-induced formation and dissolution of bonds between lattice gas atoms on nearest-neighbour sites. It is described by three (adjustable) parameters, two components of the $\boldsymbol{\lambda}$ tensor of the bonds and the jump rate of the atoms. We derive, rigorously correct within our model assumptions, the relaxation spectra for both the compressibility $s_{11}+2s_{12}$ and the shear compliance $s_{11}-s_{12}$. The two spectra are proportional to $c^2(1-c)^2$, where c is the occupation probability of a given site. The relaxation spectrum of the shear compliance is moderately broadened in comparison with a Debye relaxation, whereas the broadening of the spectrum of the compressibility is significant. The results are applicable to the Zener relaxation in both interstitial and substitutional alloys.

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Appendix A. The presence of the volume V in (5) and (6)

We consider a cube of volume V (a cube for reasons of simplicity). In this case, a true displacement x that corresponds to $\tilde{\epsilon}$ is $x=\tilde{\epsilon}V^{\frac{1}{3}}$, and a true force f that corresponds to $\tilde{\sigma}$ is $f=\tilde{\sigma}V^{\frac{2}{3}}$. The complex displacement–force relationship is then

$$x(\omega)=\alpha(\omega)f(\omega) \tag{A1}$$

where $\alpha(\omega)=\tilde{\sigma}(\omega)/V^{\frac{1}{3}}$. The free enthalpy Vg stored in V in the presence of a static $f(\omega=0)$ is given by $Vg=\frac{1}{2}V\tilde{s}^2(\omega=0)\tilde{\sigma}(\omega=0)=\frac{1}{2}\alpha(\omega=0)f^2(\omega=0)$. According to [30], the relationship between the correlation function $\langle x(t)x(t=0)\rangle$ and the imaginary part $\alpha''(\omega)$ of $\alpha(\omega)$ is described by the equation

$$\alpha''(\omega)=\frac{\omega}{2k_BT}\int_{-\infty}^{\infty}\langle x(t=0)x(t)\rangle \mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t \tag{A2}$$

in which V does not appear. Expressing now $\alpha''(\omega)$ again by $\tilde{s}''(\omega)$, and $\tilde{x}$ by $\tilde{\epsilon}(\omega)$, we end up with (5) where V shows up. Finally, the presence of V in (6) follows in the same way as its presence in (5).

Appendix B. The Snoek relaxation of $s_{11}-s_{12}$

We discuss the Snoek relaxation of $s_{11}-s_{12}$ for n octahedral interstitials in a bcc metal with N_A atoms [1, 2]. The volume per metal atom is v_0, and the interstitial concentration

$c_I = n/N_A$ is small for reasons of simplicity. There are octahedral sites of types x, y and z, and the numbers of interstitials on these sites are n_x, n_y and n_z. The expectation value for each of these numbers if $n/3$, so that n_x, n_y and n_z deviate from their expectation value by $\Delta n_x = n_x - n/3$, $\Delta n_y = n_y - n/3$ and $\Delta n_z = n_z - n/3$. Using $\boldsymbol{\lambda}$ tensors as in (1), the strain ϵ_{ij} caused by the interstitials can be described by

$$\epsilon_{ij} = (\Delta n_x/N_A)\lambda_{ij}^{(x)} + (\Delta n_y/N_A)\lambda_{ij}^{(y)} + (\Delta n_z/N_A)\lambda_{ij}^{(z)}. \tag{B1}$$

The definition of the $\boldsymbol{\lambda}$ tensors and the above expression for the strain ϵ_{ij} agree with the conventional notation [1, 2].

Using the orthogonal and normalized strain $\tilde{\epsilon}^{(2)}$ as in (11), and proceeding identically as in section 3, the correlation function for $\tilde{\epsilon}^{(2)}$ is given by (see (13))

$$\langle\tilde{\epsilon}^{(2)}(t)\tilde{\epsilon}^{(2)}(t=0)\rangle = \frac{(\lambda_1-\lambda_2)^2}{N_A^2}\{\langle\Delta n_x(t)\Delta n_x(t=0)\rangle - \langle\Delta n_x(t)\Delta n_y(t=0)\rangle\} \tag{B2}$$

where $\langle\Delta n_x(t)\Delta n_x(t=0)\rangle$ and $\langle\Delta n_x(t)\Delta n_y(t=0)\rangle$ are correlation functions of Δn_x and Δn_y, respectively.

We discuss only the total relaxation so that, according to (6), it suffices to calculate the time-independent correlation amplitudes $\langle\Delta n_x^2\rangle$ and $\langle\Delta n_x\Delta n_y\rangle$. These amplitudes are themselves correlated. Consider the sum $\Delta n_x + \Delta n_y + \Delta n_z$, which is zero. From the expectation value of the square of this sum, we yield $3\langle\Delta n_x^2\rangle + 6\langle\Delta n_x\Delta n_y\rangle = 0$, accounting for the fact that, for instance, $\langle\Delta n_x^2\rangle = \langle\Delta n_y^2\rangle$ and $\langle\Delta n_x\Delta n_y\rangle = \langle\Delta n_x\Delta n_z\rangle$. Accordingly, we find $\langle\Delta n_x\Delta n_y\rangle = -\frac{1}{2}\langle\Delta n_x^2\rangle$, so that (B2) can be rewritten as

$$\langle\tilde{\epsilon}^{(2)}(t)\tilde{\epsilon}^{(2)}(t)\rangle = \tfrac{3}{2}[(\lambda_1-\lambda_2)^2/N_A^2]\langle\Delta n_x^2\rangle. \tag{B3}$$

To determine $\langle\Delta n_x^2\rangle$, we consider that the n interstitials occupy three different types of site, where the probability for occupying a site of type x (or y or z) is $r = \frac{1}{3}$. Therefore, $\langle\Delta n_x^2\rangle = r(1-r)n = \frac{2}{9}n$, as long as $c_I = n/N_A \ll 1$ [33]. From this relation, and from (B3) and (6), we regain the familiar literature result [1, 2]

$$\Delta\tilde{s}^{(2)} = \Delta(s_{11}-s_{12}) = (1/3k_BT)(nV/N_A^2)(\lambda_1-\lambda_2)^2 = (c_I v_0/3k_BT)(\lambda_1-\lambda_2)^2. \tag{B4}$$

Appendix C. Correlation amplitudes in the $\boldsymbol{k}$ space

The correlation amplitudes of products of $\Delta c(\boldsymbol{k})$ can be traced to correlation amplitudes of products of the occupation probabilities $\Delta c(\boldsymbol{R})$ (we omit the time variable t since all product terms in the correlation amplitudes hold for the same time). We discuss $\langle\Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle$ first. According to (14), this quantity can be written as

$$\langle\Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle = \frac{1}{N^2}\sum_{\boldsymbol{R}}\sum_{\boldsymbol{R}'}\langle\Delta c(\boldsymbol{R})\Delta c(\boldsymbol{R}')\rangle\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}'} \tag{C1}$$

Defining $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ (plus $\boldsymbol{R}_3$ and $\boldsymbol{R}_4$ later) as the positions of different sites, and using the identity

$$\langle\Delta c(\boldsymbol{R})\Delta c(\boldsymbol{R}')\rangle = \langle\Delta c(\boldsymbol{R}_1)\Delta c(\boldsymbol{R}_2)\rangle + \langle\{\Delta c^2(\boldsymbol{R}_1) - \Delta c(\boldsymbol{R}_1)\Delta c(\boldsymbol{R}_2)\}\rangle\delta_{\boldsymbol{R},\boldsymbol{R}'} \tag{C2}$$

we can rewrite (C1) as

$$\langle\Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle = \langle\Delta c(\boldsymbol{R}_1)\Delta c(\boldsymbol{R}_2)\rangle\delta_{\boldsymbol{k},0} + \frac{1}{N}\langle\{\Delta c^2(\boldsymbol{R}_1) - \Delta c(\boldsymbol{R}_1)\Delta c(\boldsymbol{R}_2)\}\rangle. \tag{C3}$$

The value of $\langle\Delta c^2(\boldsymbol{R}_1)\rangle$ is $c(1-c)$ [31]. This follows from the two values $1-c$ and $-c$ that $\Delta c(\boldsymbol{R}_1)$ has with the probabilities c and $1-c$, respectively. For a fluctuating total number

of lattice gas atoms, the situation discussed by Krivoglaz [31], the occupation probabilities of different sites are uncorrelated, so that $\langle \Delta c(\boldsymbol{R}_1)\Delta c(\boldsymbol{R}_2)\rangle = 0$. This yields the result of (16), valid for all $\boldsymbol{k}$ including $\boldsymbol{k} = \boldsymbol{0}$. On the other hand, the constraint of a fixed total number of atoms causes a correlation in the occupation probabilities of different sites. To demonstrate this, we assume first site $\boldsymbol{R}_1$ being occupied (with probability c). In this case, the number of lattice gas atoms which occupy the remaining $N-1$ sites is $Nc-1$, so that the occupation probability of site $\boldsymbol{R}_2$ is $(Nc-1)/(N-1)$, which differs from c. On the other hand, if site $\boldsymbol{R}_1$ is unoccupied (with probability $1-c$), the occupation probability that follows for site $\boldsymbol{R}_2$ is $Nc/(N-1)$. These occupation probabilities for site $\boldsymbol{R}_2$ lead to $\langle \Delta c(\boldsymbol{R}_1)\Delta c(\boldsymbol{R}_2)\rangle = -c(1-c)/(N-1)$, yielding, according to (C3), $\langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle = 0$ for $\boldsymbol{k} = \boldsymbol{0}$ (as required) and $\langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle = c(1-c)/(N-1)$ for $\boldsymbol{k} \neq \boldsymbol{0}$. Therefore, it is seen that the constraint of a fixed total number of lattice gas atoms changes $\langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle$ for $\boldsymbol{k} \neq \boldsymbol{0}$ insignificantly in the limit $N \to \infty$.

In a similar way, we can derive the relation

$$\begin{aligned}\langle \{\Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\}^2\rangle &- \langle \Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\Delta c(\boldsymbol{k}_2)\Delta c(-\boldsymbol{k}_2)\rangle \\ &= \frac{1}{N^2}\langle \{\Delta c^2(\boldsymbol{R}_1) - \Delta c(\boldsymbol{R}_1)\Delta c(\boldsymbol{R}_2)\}\{\Delta c^2(\boldsymbol{R}_3) - \Delta c(\boldsymbol{R}_3)\Delta c(\boldsymbol{R}_4)\}\rangle \qquad \text{(C4)}\end{aligned}$$

where we define $\boldsymbol{k}_1 \neq \boldsymbol{k}_2$ and discuss, for reasons of simplicity, only the case $\boldsymbol{k}_1 \neq \boldsymbol{0}$ and $\boldsymbol{k}_2 \neq \boldsymbol{0}$. For a fluctuating number of atoms, where different sites are uncorrelated, the expectation value of (C4) is $\langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\rangle^2 = c^2(1-c)^2/N^2$, the result we use in subsection 4.3. However, it is also seen that the constraint of a fixed number of atoms changes this result only by an additional term which is a factor of $1/N$ smaller, so that this constraint is again insignificant in the limit $N \to \infty$.

Finally, we present the relation

$$\begin{aligned}\langle \Delta c(\boldsymbol{k})\Delta c(-\boldsymbol{k})\Delta c(\boldsymbol{k}')\Delta c(-\boldsymbol{k}')\rangle \\ = \frac{1}{N^3}\{c(1-c) - 6c^2(1-c)^2\} + \frac{1}{N^2}c^2(1-c)^2(1+\delta_{\boldsymbol{k},\pm\boldsymbol{k}'}) \qquad \text{(C5)}\end{aligned}$$

holding, for reasons of simplicity, only for a fluctuating number of atoms (in this case, $\boldsymbol{k}$, and/or $\boldsymbol{k}'$ can also be zero). Because the factor $1/N^3$ in the first term of the right-hand side (against the factor $1/N^2$ in the second term), the difference between $\langle \Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\Delta c(\boldsymbol{k}_2)\Delta c(-\boldsymbol{k}_2)\rangle$ and $\langle \Delta c(\boldsymbol{k}_1)\Delta c(-\boldsymbol{k}_1)\rangle^2 = c^2(1-c)^2/N^2$ is insignificant in the limit $N \to \infty$. This fact is used in subsection 4.3 to neglect, for instance, the second sum on the right-hand side of (31).

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