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General linear response analysis of anelasticity

V BALAKRISHNAN
Reactor Research Centre, Kalpakkam 603 102

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Abstract. Linear response theory is used to express the anelastic response (creep function and generalized compliance) of a system under an applied stress, in terms of the equilibrium strain auto-correlation. These results extend an earlier analysis to cover inhomogeneous stresses and the tensor nature of the variables. For anelasticity due to point defects, we express the strain compactly in terms of the elastic dipole tensor and the probability matrix governing dipole re-orientation and migration. We verify that re-orientations contribute to the deviatoric strain alone (Snoek, Zener, etc. effects), while the dilatory part arises solely from the long-range diffusion of the defects under a stress *gradient* (the Gorsky effect). Our formulas apply for arbitrary orientational multiplicity, specimen geometry, and stress inhomogeneity. The subsequent development of the theory in any given situation then reduces to the modelling of the probability matrix referred to. In a companion paper, we apply our formalism to work out in detail the theory of the Gorsky effect (anelasticity due to long-range diffusion) for low interstitial concentrations, as an illustration of the advantages of our approach to the problem of anelastic relaxation.

Keywords. Linear response theory; anelastic relaxation; compliance; elastic dipole; re-orientation; diffusion.

1. Introduction

In an earlier paper (Balakrishnan *et al* 1978), referred to as BDV hereafter, a formalism was developed for mechanical response (specifically, anelasticity) based on the application of linear response theory (LRT). The static and dynamic response functions (creep function and complex compliance) for an isotropic system subjected to a homogeneous uniaxial stress were expressed in terms of the autocorrelation function of the strain fluctuations in equilibrium, i.e., under zero applied stress. The origin of the fluctuations was traced to the randomness inherent in the motion of the point defects giving rise to anelastic behaviour, and a stochastic theory based on a dynamical equation of motion for the strain was developed. The formal similarity of this equation with the generalized Langevin equation for the Brownian motion of a particle in a medium with a 'memory' was brought out, and a number of results were established; the fluctuation-dissipation theorem for anelasticity, moment theorems for the power spectrum of the fluctuations, expressions for the parameters of phenomenological network models of anelasticity in terms of average values of the underlying microscopic variables, etc. As a test of some of the ideas developed in the formalism, the creep function and compliance in the case of the Snoek effect (due to the re-orientation of the elastic dipoles associated with interstitial impurities in bcc metals, e.g., carbon in α-iron) were determined *ab initio*, via an explicit evaluation of the strain autocorrelation. This was done by a simple stochastic technique, under

the assumption that the random jumps of the interstitial atoms from site to site are described by a stationary Markov process.

The treatment of mechanical response (at least at the level of anelasticity) has thus been brought in line with similar formalisms for magnetic and dielectric response, among others. In addition, a number of lines along which the formalism required generalization was indicated in BDV. In the present paper, we address ourselves to such a task: we derive the most general expression within the framework of LRT for the static and dynamic mechanical response functions, under the application of a stress field of any spatial and temporal variation, taking into account the tensor character of the stress and strain. Going over to anelasticity caused by point defects (elastic dipoles), we carry out the evaluation of the equilibrium strain autocorrelation in terms of appropriate quantities. Subsequently, in Balakrishnan (1978) (following paper), we work out the theory of the Gorsky effect (anelasticity due to long-range diffusion), to complement the theory of the Snoek effect (anelasticity due to defect re-orientation) presented in BDV, in order to illustrate the power of the present approach to such problems, besides providing an application of current interest.

A summary of the paper is as follows. In § 2, we apply LRT to the problem at hand, the results being embodied in eqs (3) and (6). In § 3, we evaluate the strain autocorrelation required in terms of the elastic dipole tensor corresponding to point defects and the effective time-development operator (or probability matrix) that controls the re-orientation of the elastic dipoles and their long-range diffusion. (The details of the calculation are given in the Appendix.) The result is the expression in (13). The saturation value of the anelastic strain under a constant load is deduced from this, to provide a general formula for the 'relaxation strength' (eq. (17) from which various special cases can be read off. In § 4, the strain response is separated into its dilatory and deviatoric parts (eq. 21), and we establish the following (known) results rigorously and in general. The deviatoric strain arises solely from the re-orientation of the elastic dipoles (i.e., the Snoek effect, Zener relaxation, etc.); the corresponding relaxation strength is a measure of the 'anisotropy' (or departure from cubic symmetry) of the elastic dipole (Nowick and Berry 1972). On the other hand, the dilatory part of the strain, i.e., the Gorsky effect, depends only on the 'size effect' introduced by the defects (i.e., on the trace of the corresponding dipole tensor), and is non-vanishing only if the applied stress is spatially inhomogeneous. The subsequent development of the theory in any given situation then reduces to the modelling or determination of the probability matrix referred to in the following. Typical approaches to this aspect of the problem have been presented elsewhere: for the case of re-orientation, in BDV and in Balakrishnan and Balakrishnan (1978); for the case of diffusion, in the paper following.

2. Application of linear response theory

We begin with a system in equilibrium at $t = -\infty$, that is described by a Hamiltonian $\mathcal{H}_0$. The equilibrium is disturbed by the application of a space- and time-dependent stress that alters the Hamiltonian to

$$\mathcal{H} = \mathcal{H}_0 - \int_V d\mathbf{R}' \, \epsilon_{kl}(\mathbf{R}') \, \sigma_{kl}(\mathbf{R}', t), \tag{1}$$

where V is the volume of the sample, and the subscripts are Cartesian indices. We regard ϵ, σ, etc. as classical variables. LRT (Kubo 1966; see also BDV) gives for the strain response at time t the expression

$$\langle \epsilon_{ij}(\mathbf{R}, t) \rangle = \langle \epsilon_{ij}(\mathbf{R}) \rangle_{\text{eq}} + \beta \int_{-\infty}^{t} dt' \int_V d\mathbf{R}' \, \sigma_{kl}(\mathbf{R}', t') \times \langle \epsilon_{ij}(\mathbf{R}, t) \, \dot{\epsilon}_{kl}(\mathbf{R}', t') \rangle_{\text{eq}}, \tag{2}$$

where $\beta = 1/k_B T$ and the dot denotes a time derivative. In the cases of interest to us, the equilibrium average of the strain may be taken to be zero. Further, if the equilibrium distribution of the defects causing the strain is uniform throughout the sample, the strain ϵ is independent of the co-ordinate $\mathbf{R}$, and this remains so in the presence of a uniform applied stress.

In a creep experiment, a time-independent stress is applied from $t=0$ onwards. The stationarity property of the equilibrium autocorrelation in (2) then gives

$$\langle \epsilon_{ij}(\mathbf{R}, t) \rangle = \beta \int d\mathbf{R}' \, \sigma_{kl}(\mathbf{R}') \, [\langle \epsilon_{ij}(\mathbf{R}, 0) \, \epsilon_{kl}(\mathbf{R}', 0) \rangle_{\text{eq}} - \langle \epsilon_{ij}(\mathbf{R}, t) \, \epsilon_{kl}(\mathbf{R}', 0) \rangle_{\text{eq}}]. \tag{3}$$

The determination of the creep function reduces now to the actual evaluation of the required autocorrelation functions in each given instance. In a dynamic experiment (e.g., internal friction measurement, ultrasonic attenuation, etc.), on the other hand, we require the response to an applied stress field

$$\sigma_{kl}(\mathbf{R}, t) = \text{Re} \, [\sigma_{kl}(\mathbf{R}) \exp(-i\omega t)], \tag{4}$$

that perturbs the initial state of equilibrium. Integrating by parts over t' in (2) with the help of the stationarity property once again, we obtain the strain response* in terms of a generalized compliance J as follows:

$$\langle \epsilon_{ij}(\mathbf{R}, t) \rangle = \text{Re} \left[\int d\mathbf{R}' \, \sigma_{kl}(\mathbf{R}') \, J_{ijkl}(\mathbf{R}, \mathbf{R}', \omega) \exp(-i\omega t) \right], \tag{5}$$

where

$$J_{ijkl}(\mathbf{R}, \mathbf{R}', \omega) = \beta \left[\langle \epsilon_{ij}(\mathbf{R}, 0) \, \epsilon_{kl}(\mathbf{R}', 0) \rangle_{\text{eq}} + i\omega \int_0^{\infty} dt' \exp(-i\omega t') \langle \epsilon_{ij}(\mathbf{R}, t') \, \epsilon_{kl}(\mathbf{R}', 0) \rangle_{\text{eq}} \right]. \tag{6}$$

The complete solution to the problem in any given situation is then represented by the evaluation of the integral

$$F_{ij}(\mathbf{R}, \omega) = \int d\mathbf{R}' \, \sigma_{kl}(\mathbf{R}') \, J_{ijkl}(\mathbf{R}, \mathbf{R}', \omega). \tag{7}$$

*Equation (5) is very clearly the non-transient response, because an infinite interval of time has elapsed since the stress was switched on at $t = -\infty$. Otherwise the strain will have other frequency components as well—or, equivalently, '$J(\omega)$' must itself have time-dependence.

3. Anelasticity due to point defect motion

We are interested in applying the above formalism to problems in which point defects (interstitials, dumb-bell pairs, etc.) cause local internal strains described by elastic dipoles, whose stress-assisted random motion leads to anelastic relaxation and associated effects. Each elastic dipole is represented by the strain tensor $\lambda_{ij}^{(n)}$, where $n=1, 2, \ldots, r$ stands for one of the r possible orientations of the dipole (Nowick and Berry 1972). In the absence of an external stress, these are equivalent orientations, equally populated by the dipoles at any given temperature. Under the action of an applied stress field, the originally degenerate energy levels corresponding to the different orientations are split up, and the system relaxes towards a population distribution determined by the split spectrum. If, in addition, there is a spatial variation of the stress across the sample, an initially uniform dispersion of elastic dipoles will diffuse to form a concentration gradient that compensates for the stress gradient to produce a minimum free energy configuration. Both these effects (preferential reorientation and diffusion) lead to anelasticity, and our treatment will encompass them in a unified manner, being a generalization of the approach developed in BDV.

Let $C_n(\mathbf{R})$ be the instantaneous concentration of elastic dipoles in orientation n in an infinitesimal volume element at the point $\mathbf{R}$. If C is the average equilibrium concentration (molefraction) of dipoles of all orientations, the relative concentration $X_n = C_n/C$ satisfies the normalization condition

$$V^{-1}\int d\mathbf{R}\sum_{n=1}^{r} X_n(\mathbf{R}) = 1, \tag{8}$$

at all times, if the total number of dipoles is conserved. The strain is related to the dipole concentration by the constitutive relation

$$\epsilon_{ij}(\mathbf{R}) = C\sum_{n=1}^{r}\lambda_{ij}^{(n)}\left[X_n(\mathbf{R}) - \frac{1}{r}\right], \tag{9}$$

the subtraction ensuring that $\langle\epsilon\rangle_{\text{eq}}$ vanishes. As in BDV, we regard $X_n(\mathbf{R})$ as a stochastic variable, leading to fluctuations in the strain both in the presence and in the absence of an applied stress, as the dipoles randomly change their orientations and positions. In order to study this random motion quantitatively (specifically, to compute the strain autocorrelation), we introduce the set of stochastic states $\{|n, \mathbf{R})\}$ where $n = 1, 2, \ldots, r$ and $\mathbf{R} \in V$. The *a priori* probability of occupation (by an elastic dipole) of the state $|n, \mathbf{R})$, in the absence of an applied stress, is given by (see the Appendix)

$$p(n, \mathbf{R})\, d\mathbf{R} = d\mathbf{R}/Vr. \tag{10}$$

In the absence of the applied stress, the time dependence of the stochastic variable $X_n(\mathbf{R})$ is controlled by a time evolution operator that we denote by $P^{\text{eq}}(t)$: thus

$$\epsilon_{ij}(\mathbf{R}, t) = P^{\text{eq}}(t)\ \epsilon_{ij}(\mathbf{R}, 0). \tag{11}$$

The matrix element $(n_1, \mathbf{R}_1 | P^{\text{eq}}(t) | n_2, \mathbf{R}_2)$ represents the conditional probability that a dipole in the state $|n_1, \mathbf{R}_1)$ at $t = 0$ evolves into the state $|n_2, \mathbf{R}_2)$ in time t.

The strain autocorrelation required to write down the mechanical response of the system is then defined in terms of the stochastic states in a manner analogous to that of BDV. We have

$$\langle \epsilon_{ij}(\mathbf{R}, t)\, \epsilon_{kl}(\mathbf{R}', 0)\rangle_{\mathrm{eq}} = \sum_{n_1} \sum_{n_2} \int d\mathbf{R}_1 \int d\mathbf{R}_2\, p(n_1, \mathbf{R}_1)$$

$$\cdot \frac{(n_1, \mathbf{R}_1 \mid \epsilon_{kl}(\mathbf{R}', 0) \mid n_1, R_1)}{(n_1, \mathbf{R}_1 \mid n_1, \mathbf{R}_1)} (n_1, \mathbf{R}_1 \mid P^{\mathrm{eq}}(t) \mid n_2, \mathbf{R}_2)$$

$$\cdot \frac{(n_2, \mathbf{R}_2 \mid \epsilon_{ij}(\mathbf{R}, 0) \mid n_2, R_2)}{(n_2, \mathbf{R}_2 \mid n_2, \mathbf{R}_2)}. \tag{12}$$

This is a product of expectation values of the strain respectively in the initial and final states, together with the probability of evolution from one state to the other, summed over the final state and averaged over the initial state with the appropriate weight factor $p(n_1, \mathbf{R}_1)$. To simplify this expression, we must use a number of properties of the states $\{\mid n, \mathbf{R})\}$. These are listed, and the simplification carried out, in the Appendix. The final result is, denoting by v_0 the volume per atom of the host crystal,

$$\langle \epsilon_{ij}(\mathbf{R}, t)\, \epsilon_{kl}(\mathbf{R}', 0)\rangle_{\mathrm{eq}} = (Cv_0/r) \sum_n \sum_m \lambda_{ij}^{(n)}\, \lambda_{kl}^{(m)} \times$$

$$[(m, \mathbf{R}' \mid P^{\mathrm{eq}}(t) \mid n, \mathbf{R}) - (1/Vr)]. \tag{13}$$

The equal-time correlation is obtained trivially from (13). We need to use the orthogonality of the states and the fact that $P^{\mathrm{eq}}(0)$ is identically equal to the unit operator **1**.

We are ready, now, to deduce the formulas for the mechanical response of the system in both creep and internal friction experiments. Substituting (13) in (3), we arrive at the general answer for the time-dependent strain under a constant stress $\sigma_{kl}(\mathbf{R})$ applied from $t=0$ onwards:

$$\langle \epsilon_{ij}(\mathbf{R}, t)\rangle$$

$$= \frac{1}{r} \beta\, Cv_0 \sum_n \sum_m \lambda_{ij}^{(n)}\, \lambda_{kl}^{(m)} \int d\mathbf{R}'\, \sigma_{kl}(\mathbf{R}')\, (m, \mathbf{R}' \mid \mathbf{1} - P^{\mathrm{eq}}(t) \mid n, \mathbf{R}) \tag{14}$$

$$= \frac{1}{r} \beta\, Cv_0 \sum_n \lambda_{ij}^{(n)} \left[\lambda_{kl}^{(n)}\, \sigma_{kl}(\mathbf{R}) - \sum_m \lambda_{kl}^{(m)} \right.$$

$$\left. \int d\mathbf{R}'\, \sigma_{kl}(\mathbf{R}')\, (m, \mathbf{R}' \mid P^{\mathrm{eq}}(t) \mid n, R) \right]. \tag{15}$$

Similarly, we find for the response to an applied time-dependent stress field of frequency ω (see (4)–(7)).

$$F_{ij}(\mathbf{R}, \omega) = \frac{1}{r}\beta C v_0 \sum_n \lambda_{ij}^{(n)} \Big[\lambda_{kl}^{(n)} \sigma_{kl}(\mathbf{R}) + i\omega \sum_m \lambda_{kl}^{(m)} \times$$

$$\int d\mathbf{R}' \, \sigma_{kl}(\mathbf{R}') \int_0^\infty dt' \exp(i\omega t') (m, \mathbf{R}' \mid P^{\mathrm{eq}}(t') \mid n, \mathbf{R}) \Big]. \qquad (16)$$

Equations (15) and (16) represent the most general form of solution to the problem at hand, containing the effects of both re-orientation and long-range diffusion of the defects (elastic dipoles). It is worth recalling the conditions under which the above results are valid. These are: (i) linear response to the applied stress; (ii) conservation of the total number of defects, i.e., no defect reactions or diffusion of defects into or out of the specimen; (iii) no defect-defect interactions; (iv) a single energy level for all the r orientations of a dipole in the absence of an applied stress. It is possible to relax the latter three assumptions to varying degrees and to work out a more involved formalism. The extension to nonlinear response is a much deeper question, and different methods have to be appealed to, depending on the particular problem (see, for instance, Venkataraman and Balakrishnan 1977).

To proceed further in any given situation, the probability matrix $P^{\mathrm{eq}}(t)$ must be specified or modelled. However, the asymptotic ($t \to \infty$) limit of this quantity is obtained readily on physical grounds: we expect that the matrix element connecting the initial state $|m, \mathbf{R}'\rangle$ to the final state $|n, \mathbf{R}\rangle$ becomes independent of the initial state as the elapsed time $t \to \infty$, and in fact becomes equal to the *a priori* occupation probability in equilibrium of the latter state. Using (10) for this probability, we find that the saturation value of the strain under a constant applied stress is

$$\langle \epsilon_{ij}(\mathbf{R}, \infty) \rangle = \frac{1}{r}\beta C v_0 \sum_n \lambda_{ij}^{(n)} \Big[\lambda_{kl}^{(n)} \sigma_{kl}(\mathbf{R})$$

$$- \frac{1}{Vr} \sum_m \lambda_{kl}^{(m)} \int d\mathbf{R}' \, \sigma_{kl}(\mathbf{R}') \Big]. \qquad (17)$$

This is a generalized expression for the ' relaxation strength ', which is related to the change in the elastic modulus owing to the presence of the defects (dipoles). Under certain experimental conditions (such as the bending of a beam of rectangular cross section, to be considered in the next paper), the applied stress field is such that the integral on the second term on the right vanishes, leading to a particularly simple formula for the relaxation strength (see, e.g., Nowick and Berry 1972).

4. Separation of re-orientational and diffusive effects

With the help of the formalism developed above, it is easy to establish the following two important conclusions: (i) anelasticity due to long-range diffusion occurs only if the applied stress is spatially inhomogeneous across the sample, and (ii) the effect of re-orientation is probed only by the deviatoric or traceless part of the applied stress. Although it is possible to work out the case of any general crystal and defect (dipole) symmetry, it is convenient to concentrate on elastic dipoles of cubic, tetragonal, hexagonal, trigonal or orthorhombic symmetry. In all these cases the number

of independent components of the λ tensor does not exceed three, and certain properties of $\lambda_{ij}^{(n)}$ can be verified quite simply—namely, that Tr $\lambda^{(n)}$ is independent of the orientation n, and that the sum over all orientations of each component of the deviatoric part of the λ tensor vanishes. (For a complete group-theoretical treatment of the λ tensor in the case of arbitrary crystal and defect symmetry, we refer to Nowick and Heller 1965.)

Let us first write the dipole tensor as the sum of its dilatory (trace) and deviatoric (traceless) parts, i.e.,

$$\lambda_{ij}^{(n)} = \frac{1}{3}\delta_{ij}\,\mathrm{Tr}\,\lambda^{(n)} + \left(\lambda_{ij}^{(n)} - \frac{1}{3}\delta_{ij}\,\mathrm{Tr}\,\lambda^{(n)}\right)$$

$$\equiv \frac{1}{3}\delta_{ij}\,\mathrm{Tr}\,\lambda^{(n)} + \hat{\lambda}_{ij}^{(n)}. \tag{18}$$

When a tensor split up thus is contracted with another that is similarly separated the cross terms vanish. This fact is used, together with the properties of the dipole tensor stated above, to re-cast (15) for the strain response under a constant applied stress in a form that is convenient for the discussion of the underlying physical processes. During the simplification, one encounters a partial sum over the orientation states of the matrix elements of $P^{\mathrm{eq}}(t)$. Even without explicitly assuming that this operator is a direct product $P_r^{\mathrm{eq}} \otimes P_d^{\mathrm{eq}}$ of operators that act only on the orientation and position states respectively, we may use the conservation of probability to write

$$\sum_n (m, \mathbf{R}' \,|\, P^{\mathrm{eq}}(t) \,|\, n, \mathbf{R}) = \left(\mathbf{R}' \,|\, P_d^{\mathrm{eq}}(t) \,|\, \mathbf{R}\right), \tag{19}$$

and similarly

$$\int d\mathbf{R}\, (m, \mathbf{R}' \,|\, P^{\mathrm{eq}}(t) \,|\, n, \mathbf{R}) = \left(m \,|\, P_r^{\mathrm{eq}}(t) \,|\, n\right). \tag{20}$$

These equations serve as definitions of the matrix elements of effective time development operators P_d^{eq} and P_r^{eq} controlling respectively the long-range diffusion and the re-orientation of the dipoles.* Employing (18) and (19) to simplify (15), we obtain finally

$$\langle \epsilon_{ij}(\mathbf{R}, t)\rangle = \frac{1}{r}\beta\, C v_0 \sum_n \sum_m \hat{\lambda}_{ij}^{(n)}\, \hat{\lambda}_{kl}^{(m)}$$

$$\int d\mathbf{R}'\, \hat{\sigma}_{kl}(\mathbf{R}')\, (m, \mathbf{R}' \,|\, \mathbf{1} - P^{\mathrm{eq}}(t) \,|\, n, \mathbf{R})$$

$$+ \frac{1}{9}\beta\, C v_0\, (\mathrm{Tr}\,\lambda)^2\, \delta_{ij} \int d\mathbf{R}'\, \mathrm{Tr}\,\sigma(\mathbf{R}')\, (\mathbf{R}' \,|\, \mathbf{1} - P_d^{\mathrm{eq}}(t) \,|\, \mathbf{R}), \tag{21}$$

*It might appear at first sight that eqs (19) and (20) are valid only if the operator P^{eq} is a direct product of operators, $P_r^{\mathrm{eq}} \otimes P_d^{\mathrm{eq}}$, and therefore incorrect for $|\mathbf{R} - \mathbf{R}'|$ of the order of a single atomic jump distance, because orientations and sites are generally interlinked: from a given orientation, the dipole may be able to go only to a subset of possible orientations in a single jump, so that certain matrix elements of $P^{\mathrm{eq}}(t)$ must vanish identically for such values of $|\mathbf{R} - \mathbf{R}'|$. However, the *summation* over n in eq. (19) takes care of this problem, and the reduction is correct in all cases.

which represents also a splitting of the strain into its dilatory and deviatoric parts. The response in a dynamic experiment, (16), can be handled in a similar fashion.

We may substantiate, now, the two statements made in the beginning of this section. If the applied stress has no spatial variation across the sample, this quantity can be placed outside the integrals in (21). The first integral may be performed with the help of (20) (the matrix elements of the equilibrium probability matrix being symmetric), while the second integral vanishes on account of the orthonormality of the states and the conservation of probability. The strain response is thus spatially homogeneous, as expected, and is given by

$$\langle \epsilon_{ij}(t) \rangle = \frac{1}{r} \beta v_0 C \sum_n \sum_m \hat{\lambda}_{ij}^{(n)} \hat{\lambda}_{ij}^{(m)} \hat{\sigma}_{kl} (m \,|\, 1 - P_r^{\mathrm{eq}}(t) \,|\, n)$$

$$= \frac{1}{r} \beta C v_0 \sum_n \hat{\lambda}_{ij}^{(n)} \left[\hat{\lambda}_{kl}^{(n)} - \sum_m \hat{\lambda}_{kl}^{(m)} (m \,|\, P_r^{\mathrm{eq}}(t) \,|\, n) \right] \hat{\sigma}_{kl}. \tag{22}$$

This result involves only the re-orientation of the dipoles, and the corresponding strain is purely deviatoric.* This establishes the first of the two assertions made earlier. The second is also manifest in (21), for the dilatory term in that equation involves no reference to re-orientations at all, being dependent on $P_d^{\mathrm{eq}}(t)$. The known fact that the long-range diffusion of the defects yields information only on the overall 'size' of the defect as quantified in $\mathrm{Tr}\lambda$, while the re-orientation leads to information on the anisotropy of the dipole tensor (i.e., on differences between the principal components), is also evident from (21).

We conclude with a few words on the modelling of the probability matrix $P^{\mathrm{eq}}(t)$, or the effective time development operator, in specific situations. In cases involving dipole re-orientation alone, there is a simple semi-phenomenological approach possible, based on stochastic considerations (see BDV). This is based on the assumption that the jumps of the point defects (that lead to the re-orientations of the dipoles) are governed by a stationary Markov process, so that $P_r^{\mathrm{eq}}(t)$ can be written in the form $\exp(W^{\mathrm{eq}}t)$ (Anderson 1954), W^{eq} being a (time-independent) $(r \times r)$ matrix called the transition matrix. Its off-diagonal elements are just the various re-orientation frequencies. On the other hand, a more fundamental approach to the relaxation problem is afforded by a density matrix formalism (Balakrishnan and Balakrishnan 1978) that is similar to the one used in the study of magnetic relaxation. This method enables us to relate the anelastic relaxation time (and hence the 're-orientation frequency') directly to the strength and correlation time of the defect hopping term in the total Hamiltonian of the system concerned. Turning to the case of relaxation owing to the long-range diffusion of point defects (the Gorsky effect), somewhat different techniques are required. This problem is studied in the paper that follows.

Appendix

The strain autocorrelation function

We shall indicate here how the formal expression of (12) for the auto-correlation reduces to that of (13). It is necessary, first, to list some properties of the set of states

*Anelasticity due to dipole re-orientation persists, of course, when the applied stress is spatially inhomogeneous. The first term on the right in (21) covers this situation too.

$\{|n, \mathbf{R})\}$. These states are labelled by the (discrete) orientation index n and the (continuous) position co-ordinate $\mathbf{R}$. The latter circumstance necessitates some care in normalization factors (e.g., dimensions, etc.). The orthogonality relation is

$$(n, \mathbf{R}\,|\,m, \mathbf{R}') = \delta_{nm}\delta(\mathbf{R}-\mathbf{R}'), \tag{A.1}$$

together with the normalization

$$(n, \mathbf{R}\,|\,n, \mathbf{R}) = V^{-1}, \tag{A.2}$$

(obtained by going to continuous values of $\mathbf{R}$ from a discrete set). It is useful to remember also that

$$\int d\mathbf{R}_1\, \delta(\mathbf{R}_1-\mathbf{R})\delta(\mathbf{R}_1-\mathbf{R}') = \delta(\mathbf{R}-\mathbf{R}'), \tag{A.3}$$

and

$$\int d\mathbf{R}_1\, \delta(\mathbf{R}_1-\mathbf{R})\, \delta(\mathbf{R}_1-\mathbf{R}) = V^{-1}. \tag{A.4}$$

The completeness relation is

$$\int d\mathbf{R} \sum_{n=1}^{r} |n, \mathbf{R})\,(n, \mathbf{R}| = \mathbf{1}. \tag{A.5}$$

We require the *a priori* probability density $p(n, \mathbf{R})$ and the matrix elements of the operator $X_n(\mathbf{R})$. The former is, by definition,

$$p(n, \mathbf{R}) = (n, \mathbf{R}\,|\exp(-\beta\mathcal{H}_0)\,|n, \mathbf{R})/\mathrm{Tr}\exp(-\beta\mathcal{H}_0), \tag{A.6}$$

where the trace stands for a summation over n and $\mathbf{R}$ of the diagonal matrix elements of the operator concerned. Since we have assumed that all the orientations are equivalent and that the dipole concentration is uniform in equilibrium, we have

$$p(n, \mathbf{R}) = (n, \mathbf{R}\,|\,n, \mathbf{R})/\mathrm{Tr}\,\mathbf{1} = (Vr)^{-1}, \tag{A.7}$$

the expression quoted in (10). Turning to the operator $X_n(\mathbf{R})$, we require a diagonal representation that explicitly indicates a dipole in orientation n at the point $\mathbf{R}$, i.e., we must have

$$(m, \mathbf{R}'\,|\,X_n(\mathbf{R})\,|\,m, \mathbf{R}') = \delta_{mn}\delta(\mathbf{R}-\mathbf{R}'). \tag{A.8}$$

It is deduced easily from this that the general matrix element of $X_n(\mathbf{R})$ is

$$(l, \mathbf{R}''\,|\,X_n(\mathbf{R})\,|\,m, \mathbf{R}') = V\delta_{mn}\,\delta_{lm}\delta(\mathbf{R}-\mathbf{R}')\,\delta(\mathbf{R}'-\mathbf{R}''). \tag{A.9}$$

Returning to (12) for the correlation function, we substitute for the strain the constitutive relation (9) and use the properties listed above. The result is* (with $v_0 = V/N$ = atomic volume of the host crystal).

*The ubiquitous overall factor Cv_0 arises as follows. Our states $|n, \mathbf{R})$ refer to *individual* dipoles, and should be appropriately normalized (we have not indicated this explicitly). A more straightforward procedure is to work in a direct product space of all the N_d defects. (In the case of pure re-orientation alone, this is an easily visualized r^{N_d}-dimensional vector space). The expression for the strain autocorrelation then turns out to have an overall factor VC^2/N_d. Since $C = N_d/N$ where N is the total number of atoms of the host crystal, we may write this factor as Cv_0 where $v_0 = V/N$ is the volume per atom of the host crystal. It is appropriate to comment here on similar factors in the results of BDV. All expressions involving the factor VC^2 in that paper should be replaced by VC^2/N_d. However, since VC has further been incorrectly set equal to v_0, instead of v_0N_d, this error cancels out and the final expressions of BDV in terms of v_0C happen to be correct. The author is grateful to R Balakrishnan for clarifying these points.

$$\langle \epsilon_{ij}(\mathbf{R}, t)\epsilon_{kl}(\mathbf{R}', 0)\rangle_{\text{eq}} = (Cv_0/r)\sum_{n_1}\sum_{n_2}\Big[\lambda_{kl}^{(n_1)}\lambda_{ij}^{(n_2)} \times$$

$$(n_1, \mathbf{R}' \,|\, P^{\text{eq}}(t) \,|\, n_2, \mathbf{R}) - (1/Vr)\sum_m \lambda_{kl}^{(m)}\lambda_{ij}^{(n_2)} \int d\mathbf{R}_1 \times$$

$$(n_1, \mathbf{R}_1 \,|\, P^{\text{eq}}(t) \,|\, n_2, \mathbf{R}) - (1/Vr)\sum_n \lambda_{kl}^{(n_1)}\lambda_{ij}^{(n)} \int d\mathbf{R}_2 \times$$

$$(n_1, \mathbf{R}' \,|\, P^{\text{eq}}(t) \,|\, n_2, \mathbf{R}_2) + (1/Vr)^2 \sum_n \sum_m \lambda_{ij}^{(n)}\lambda_{kl}^{(m)} \times$$

$$\int d\mathbf{R}_1 \int d\mathbf{R}_2 \, (n_1, \mathbf{R}_1 \,|\, P^{\text{eq}}(t) \,|\, n_2, \mathbf{R}_2)\Big]. \tag{A.10}$$

However, since $p(n, \mathbf{R})$ is actually independent of n and $\mathbf{R}$, (see (A.7)), detailed balance implies that

$$(n. \mathbf{R} \mid P^{\text{eq}}(t) \mid m, \mathbf{R}') = (m, \mathbf{R}' \mid P^{\text{eq}}(t) \mid n, \mathbf{R}). \tag{A.11}$$

Further, conservation of probability yields

$$\sum_n \int_V d\,\mathbf{R}\, (m, \mathbf{R}' \mid P^{\text{eq}}(t) \mid n, \mathbf{R}) = 1 \; (m = 1, \ldots r; \mathbf{R}' \in V). \tag{A.12}$$

With the help of these, we obtain finally

$$\langle\, \epsilon_{ij}\,(\mathbf{R}, t)\, \epsilon_{kl}\,(\mathbf{R}', 0)\,\rangle_{\text{eq}} = (Cv_0/r)\sum_n \sum_m \lambda_{(ij)}^{(n)}\, \lambda_{(kl)}^{(m)} \times$$

$$[(m, \mathbf{R}' \mid P^{\text{eq}}\,(t) \mid n, \mathbf{R}) - (1/Vr)], \tag{A.13}$$

the expression quoted in (13).

References

Anderson P W 1954 *J. Phys. Soc. Jpn.* **9** 316

Balakrishnan V 1978 *Pramana* **11** 389

Balakrishnan Radha and Balakrishnan V 1978 *Pramana* (to be published)

Balakrishnan V, Dattagupta S and Venkataraman G 1978 *Philos. Mag.* **A37** 65 (referred to as BDV in the text)

Kubo R 1966 *Rep. Progr. Phys.* **29** 255

Nowick A S and Heller W R 1965 *Adv. Phys.* **14** 101

Nowick A S and Berry B S 1972 *Anelastic Relaxation in Crystalline Solids* (New York: Academic Press)

Venkataraman G and Balakrishnan V 1977 in *Proc. Indo-German Seminar on Radiation Damage*, Kalpakkam (in press)