

Density matrix formalism for anelastic relaxation

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MS received 19 May 1978; revised 28 August 1978

Abstract. A density matrix formalism is developed for anelastic (mechanical) relaxation in crystalline materials with point defects characterized by elastic dipoles. The time-dependent approach to equilibrium of the strain response under the action of a constant applied stress is deduced. The formalism parallels the one used in nuclear magnetic relaxation. The anelastic relaxation time is determined as a function of the parameters occurring in the defect hopping term in the Hamiltonian. This term is responsible for the dissipation of the anelastic 'potential' energy into the host lattice. In a lengthy concluding section, the following aspects are discussed point by point: the advantages of the formalism presented, its scope and special cases; the physical implications of the expression obtained for the relaxation time; the similarities and differences between magnetic relaxation and anelastic relaxation, etc.

Keywords. Anelasticity; elastic dipole; Snoek relaxation; density matrix; relaxation time.

1. Introduction

Mechanical response experiments on an anelastic crystalline solid yield a great deal of information on the configuration and kinetics of the defects in the materials. Such information on the underlying physical processes may be extracted from both the static response (anelastic relaxation or recoverable creep) and the dynamic response (internal friction or ultrasonic attenuation) of the system to an applied stress. The subject is of considerable importance in materials science, and is characterized by lively theoretical and experimental interest (Nowick and Berry 1972; Schilling 1977).

Recently, a formalism has been developed for anelasticity on the basis of linear response theory (LRT), to exhibit the similarity of the phenomenon with magnetic response, dielectric response, etc. (Balakrishnan *et al* 1978, referred to as paper I hereafter). This takes one far beyond the phenomenological network models of mechanical behaviour as far as anelasticity is concerned. Network models (in rheology) are similar to lumped parameter electrical circuits. The simplest anelastic element is the Voigt model, consisting of a spring of modulus E connected in parallel to a Newtonian dash-pot of viscosity η . The strain response ϵ to an applied (uniaxial) stress σ is given by the solution of the first-order differential equation

$$\eta \dot{\epsilon}(t) + E \epsilon(t) = \sigma(t). \quad (1)$$

For a constant stress σ applied from $t = 0$ onwards, the strain creeps up from zero to the saturation value σ/E according to

$$\epsilon(t) = (\sigma/E) [1 - \exp(-Et/\eta)]. \quad (2)$$

The dissipative element (the dash-pot of viscosity η) controls the rate of anelastic relaxation. Going beyond such phenomenology, one recognizes that anelastic behaviour is caused by the stress-modulated motion of defects in the host material. In analogy with magnetism, the concept of an *elastic dipole* is introduced (Nowick and Berry 1972): this is the strain field characterizing the distortion of the perfect lattice by a unit concentration of point defects (which may be interstitials, or split interstitials, or mixed dumb-bell pairs, etc.). The elastic dipoles couple to the applied stress, and their subsequent motion leads to the static and dynamic phenomena observed in anelastic solids, much as in a system of elementary magnetic dipoles. Thermodynamic arguments based on the minimisation of the free energy then yield some information on the relaxation process, the relaxation strength, etc. (Nowick and Berry 1972).

The essential step forward taken in paper I was the systematic exploitation of the random nature of the motion of the elastic dipoles. This leads to expressions for the static and dynamic response functions in terms of the autocorrelation of the fluctuating strain in the *absence* of any applied stress, as may be expected in LRT. Equation (2) for the creep function is replaced, for instance, by

$$\langle \epsilon(t) \rangle = \frac{V\sigma \langle \epsilon^2 \rangle_0}{k_B T} \left[1 - \frac{\langle \epsilon(0) \epsilon(t) \rangle_0}{\langle \epsilon^2 \rangle_0} \right], \quad (3)$$

where $\langle \rangle_0$ refers to an ensemble average in the absence of applied stress. A parallel formalism based on a stochastic equation for the fluctuating microscopic strain (similar to the Langevin equation and its generalization) was also given in I. Besides relating phenomenological parameters (such as E and η introduced above) to more fundamental quantities (such as the mean squared value $\langle \epsilon^2 \rangle_0$), various theorems were also established: the fluctuation-dissipation theorem, sum rules for the moments of the power spectral density of the strain, etc. Some of the results derived were verified by a calculation of the creep function associated with Snoek relaxation—the relaxation of elastic dipoles of tetragonal symmetry in a cubic lattice (e.g., carbon interstitials in bcc α -iron). In a recent paper (Balakrishnan 1978a), the entire theory has been generalized to the case of applied stress fields of arbitrary spatial inhomogeneity. The tensor nature of ϵ and σ has been taken into account, as also the anelastic effects due to both re-orientation and diffusion (long-range migration) of the elastic dipoles. An application to the Gorsky effect has also been carried out (Balakrishnan 1978b).

There is a lacuna in the approach to the relaxation problem based on thermodynamic considerations (Nowick and Berry 1972) as well as that presented in I. In these works, the underlying re-orientation process occasioned by the jump of an interstitial atom from a given site to a neighbouring one is simply assumed to proceed at an average rate or "reorientation frequency" ν . The relaxation time then turns out to be directly proportional to ν^{-1} , the constant of proportionality

depending on the particular problem (the symmetries of the dipole and host lattice, the number of equivalent orientations, etc.). In the case of Snoek relaxation of $\langle 100 \rangle$ tetragonal elastic dipoles in a cubic lattice, for instance, the creep function is found to be given by

$$\langle \epsilon(t) \rangle = (\text{const.}) \sigma [1 - \exp(-3\nu t)]. \quad (4)$$

Nothing further (based on more fundamental considerations) is deduced regarding ν . One then assumes an Arrhenius type of temperature dependence for this quantity, namely, $\nu = \nu_0 \exp(-Q/k_B T)$, in order to compare the theory with experimental data (Nowick and Berry 1972). That nothing beyond the results of phenomenological rate theory emerges in *such* applications of the LRT-based formalism is not surprising, because nothing has been put in explicitly regarding the actual mechanisms (e.g., the dynamics of the defect atoms) that cause the transitions between the different orientation states of the elastic dipoles. This is one aspect that must be included in order to make further progress. In addition, it is evident that a complete (quantum mechanical) description of the system would be obtained only if we use the density matrix formalism. It is well known (Abragam 1961) that theories phrased in terms of transition probabilities alone tacitly assume the vanishing of the off-diagonal matrix elements of the density matrix (this is equivalent to using the random phase approximation). It is therefore necessary to complete the microscopic theory of anelastic behaviour by working out a quantum mechanical formalism beginning with a total Hamiltonian H for the system of interest and solving the master equation for the density matrix. This will yield the time-dependence of the approach to equilibrium in terms of the basic parameters occurring in H . Further, one can go over to the classical limit. Most cases of practical interest fall in this regime. The classical limit of a quantum mechanical formalism provides a systematic, first-principles approach to these problems, in addition to being a simpler approach than setting up and solving the Liouville equation for the classical density matrix.

This is the purpose of the present paper. We again use Snoek relaxation as the specific case for which the formalism is worked out, in order to facilitate comparison with I (see the comments made at the end of this section). In § 2, the different terms contributing to H are identified and suitably modelled, including the defect hopping energy that causes the dissipation of the anelastic potential energy into the lattice. In § 3, 4 and 5, the density matrix (operator) method of Abragam (1961), used so successfully in the context of NMR, is developed for the problem at hand. The relaxation time τ is related to the strength and correlation time of the defect hopping term in the Hamiltonian, via a formula that expresses τ in terms of the power spectral density of this term. In the final section, which is arranged as a series of remarks for clarity, we discuss the following points: the advantages gained by the present approach, its scope, special cases (classical versus quantum mechanical treatment of various aspects of the problem); the physical implications of the result found for τ ; the similarities between magnetic and anelastic relaxation, and the differences in the temperature dependence of the relaxation time in the two cases, etc.

Finally, we may mention here that the formalism can be modified in a straightforward manner for application to other examples of anelastic relaxation (see, e.g., Nowick and Berry 1972, and the discussion in Venkataraman and Balakrishnan

1977). In particular, the 'Hamiltonian approach' of the present paper makes it eminently suitable for application to a very important case of physical interest: relaxation in materials with sufficiently high concentrations of defects, such that defect-defect interactions play a significant role. Work in this direction is in progress on Zener relaxation in concentrated alloys, and will be reported elsewhere.

2. The Hamiltonian

In order to set up a density matrix formalism for anelastic relaxation, we have to write down first the complete Hamiltonian H for the system. As stated earlier, we shall restrict ourselves to a specific case (elastic dipoles of tetragonal symmetry in a bcc lattice) so as to be able to exhibit all formulas explicitly.

There are essentially three distinct terms in H . They are (i) the anelastic potential energy arising from the coupling of the elastic dipoles to the applied stress; (ii) the energy of the host lattice, or 'phonon bath'; and (iii) the kinetic energy originating from the hopping or jump diffusion of the interstitial defect atoms from site to site. Let us consider these in turn.

2.1. Anelastic potential energy

We consider a specimen of volume V with N host atoms and N_d defects (interstitial impurity atoms). The concentration $C = N_d/N$ is assumed to be much smaller than unity, so that defect-defect interactions may be neglected, and the defects taken to move in an uncorrelated fashion in the host lattice. Each defect is described (Nowick and Berry 1972) by an elastic dipole of tetragonal symmetry: the strain induced by a single defect is given by $(1/N)\lambda$, where λ is called the elastic dipole tensor. In the present case, the principal axis system of the tensor λ coincides with the cubic system of the host crystal. The principal axis components of λ are λ_1 , λ_2 , and $\lambda_3 = \lambda_2$ (tetragonal symmetry), and the direction in which the component is λ_1 can be used to label the orientation of the elastic dipole (figure 1). Let C_p ($p=1, 2$ or 3) represent the concentration of defects in orientation p , satisfying $C_1 + C_2 + C_3 = C$ at all instants of time. C_p is a fluctuating quantity, since the defects jump randomly from one orientation to another. Measured physical quantities are actually certain statistical averages of such random variables. In the absence of any applied stress, the three orientations will be equally populated (on the average). This is expressed by the equation $\langle C_p \rangle_0 = C/3$ ($p=1, 2, 3$). If a constant, uniaxial stress σ is applied along $[100]$ from $t=0$ onwards, the equilibrium is disturbed. The dipoles will then relax towards a new population distribution that minimises the free energy, exactly as in magnetism. It is the approach to this new state of equilibrium that manifests itself as anelastic creep, and that we desire to study. As we are concerned only with the 11-component of the strain tensor, we omit these tensor indices in all that follows. The total instantaneous strain in the material is given by

$$\epsilon = \sum_{p=1}^3 \lambda_p \left(C_p - \frac{C}{3} \right). \quad (5)$$

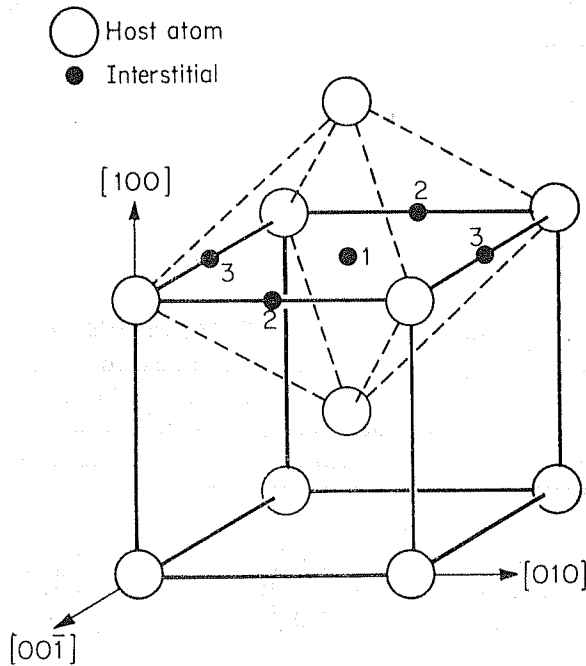


Figure 1. Sites involved in the hopping of an interstitial atom in a bcc lattice leading to Snoek relaxation under the application of an external stress. 1, 2 and 3 refer to the types of interstitial sites available, and also label the orientations of the elastic dipole associated with the defect (after Nowick and Berry 1972).

The subtraction is merely to take care of the reference level, $\langle \epsilon \rangle_0 = 0$. Using the fact that $\lambda_2 = \lambda_3$, we may re-write (5) in the form

$$\epsilon = (\lambda_1 - \lambda_2) \left(C_1 - \frac{C}{3} \right) = \frac{(\lambda_1 - \lambda_2)}{N} N_d \left(\frac{C_1}{C} - \frac{1}{3} \right). \quad (6)$$

The reason for the final equation above is as follows. To evaluate the statistical averages required, we shall take recourse to the techniques of statistical mechanics. For this, we shall introduce a Hamiltonian that is written in terms of an operator related to the strain *per defect*, as in magnetism where individual spin operators are the dynamical variables. Thus (6) is written as

$$\epsilon = \frac{(\lambda_1 - \lambda_2)}{N} \sum_{i=1}^{N_d} A_i, \quad (7)$$

where i labels the individual dipoles, and

$$\sum_{i=1}^{N_d} A_i = N_d \left(\frac{C_1}{C} - \frac{1}{3} \right). \quad (8)$$

The coupling of the elastic dipoles with the applied stress contributes to the total Hamiltonian H a term

$$H_{\sigma} = -V\sigma\epsilon = -v_0\sigma(\lambda_1 - \lambda_2) \sum_{i=1}^{N_d} A_i \quad (9)$$

where $v_0 = V/N$ is the volume per atom of the host crystal. Subsequently we shall use also the associated frequency

$$\omega_{\sigma} = v_0\sigma(\lambda_1 - \lambda_2)/\hbar \quad (10)$$

where \hbar is Planck's constant. Let us now turn to explicit representations for the various quantities (operators) concerned. (The measured strain will be a certain expectation value in the sense of statistical mechanics). Since each dipole can take on three orientations in the problem at hand, it is natural to work in a 3-dimensional vector space for *each* defect that is spanned by the (single-particle) orientation states $|p\rangle_i$ with representations

$$|1\rangle_i = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |2\rangle_i = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |3\rangle_i = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (11)$$

The states of the complete system of N_d defects are direct products of these single particle states. Correspondingly, all operators (such as A_i , H_{σ} , ϵ) have direct product representations, since no defect-defect interactions are considered. (Of course the direct product *space* continues to be of utility even when such interactions are included. This is why we elaborate on the representation, etc. at such length here). The unit operator is

$$I = \mathbf{1}_1 \otimes \mathbf{1}_2 \otimes \dots \otimes \mathbf{1}_{N_d} \quad (12)$$

where $\mathbf{1}_i$ denotes the 3×3 unit matrix acting in the space spanned by the states $|p\rangle_i$ of the i th dipole. Thus $\text{Tr } I = 3N_d$. We also have

$$A_i = \mathbf{1}_1 \otimes \dots \otimes \mathbf{1}_{i-1} \otimes (a)_i \otimes \mathbf{1}_{i+1} \otimes \dots \otimes \mathbf{1}_{N_d} \quad (13)$$

where (a) is the 3×3 matrix corresponding to an occupation number of unity for orientation 1, minus $1/3$ the unit matrix, according to (8). That is,

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} - \frac{1}{3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \frac{2}{3} & 0 & 0 \\ 0 & -\frac{1}{3} & 0 \\ 0 & 0 & -\frac{1}{3} \end{pmatrix}. \quad (14)$$

$$\text{Therefore } \text{Tr } A_i = 0 = \text{Tr } H_{\sigma}. \quad (15)$$

2.2. Host lattice energy

The corresponding contribution to H , denoted by H_L , may be written in terms of appropriate phonon co-ordinates if necessary. These operators do not affect the

orientation states, and $[H_\sigma, H_L] = 0$. The lattice is supposed to be a very large system that acts as a heat bath maintained at a temperature T_L that is the temperature of the material concerned. We use the notation

$$\beta_L = 1/k_B T_L.$$

2.3. Defect kinetic (hopping) energy

This is the term that causes the transfer of anelastic potential energy to the lattice, leading to relaxation. For simplicity, only nearest-neighbour hops (see figure 1) will be assumed, although there is no difficulty in extending the theory to other cases as well. We note that each such hop alters the dipole orientation. The contribution to H describing the hopping of a defect may be written as a direct product of two operators g and R_i , where g acts on the phonon (or host lattice) states and R_i alters the orientation state of the i th elastic dipole. The expectation value $\langle g \rangle$ represents the hopping energy of a defect. It is evident that R_i has the representation

$$R_i = \mathbf{1}_1 \otimes \dots \otimes \mathbf{1}_{i-1} \otimes (r)_i \otimes \mathbf{1}_{i+1} \otimes \dots \otimes \mathbf{1}_{N_d}, \quad (16)$$

where

$$r = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad (17)$$

so that

$$r |1\rangle = |2\rangle + |3\rangle, \text{ etc.} \quad (18)$$

The hopping term in H is thus

$$H_h = g \sum_{i=1}^{N_d} R_i. \quad (19)$$

It is easily seen that $[H_\sigma, H_h] \neq 0$, since the matrices (a) and (r) do not commute. This, together with the condition $[H_L, H_h] \propto [H_L, g] \neq 0$, is the mathematical origin of the transfer of energy from the anelastic term to the lattice bath, i.e. of the relaxation process.

After the applied stress is turned on at $t = 0$, the total Hamiltonian is thus

$$\begin{aligned} H &= H_\sigma + H_h + H_L \\ &= -v_0 \sigma (\lambda_1 - \lambda_2) \sum_i A_i + g \sum_i R_i + H_L. \end{aligned} \quad (20)$$

When the relaxation is complete, and the system is once again in equilibrium at temperature T_L , the saturation value of the strain is

$$\langle \epsilon(t = \infty) \rangle \equiv \langle \epsilon \rangle_{\text{eq}} = \text{Tr} [\epsilon \exp(-\beta_L H)] / \text{Tr} \exp(-\beta_L H). \quad (21)$$

The anelastic effects of interest occur at low stress levels, expressed more precisely by the conditions $v_0 \sigma \beta_L \ll 1$, $\langle g \rangle \beta_L \ll 1$. Equation (7) for ϵ is substituted in (21). Since $\text{Tr } A_i$ vanishes, we find (to first order in $v_0 \sigma \beta_L$)

$$\langle \epsilon \rangle_{\text{eq}} = (1/N) v_0 \sigma \beta_L (\lambda_1 - \lambda_2)^2 \sum_{i=1}^{N_d} [\text{Tr } (A_i^2) / \text{Tr } I]. \quad (22)$$

Equations (12)–(14) then easily yield

$$\langle \epsilon \rangle_{\text{eq}} / \sigma = \frac{2}{9} v_0 C \beta_L (\lambda_1 - \lambda_2)^2 \quad (23)$$

where we have written C for N_d/N , as already defined. This is the known expression for the relaxation strength in the present case (Nowick and Berry 1972; Balakrishnan *et al* 1978).

3. Elastic dipole “temperature”

It is clear from the foregoing that our problem is closely analogous to the very familiar one of magnetic relaxation. Since both H_σ and H_L commute with H in the absence of H_h , it is possible then to construct simultaneous stationary states for the two sub-systems corresponding respectively to H_σ and H_L . These may be designated as the stress bath (the analogue of the Zeeman bath) and the lattice bath. When H_h is “switched on”, neither H_σ nor H_L commutes with H , so that both $\langle H_\sigma \rangle$ and $\langle H_L \rangle$ become time-dependent. In other words, transfer of energy occurs from the stress bath to the lattice bath, via H_h . The strain relaxes from its initial value $\langle \epsilon \rangle_0 = 0$ to the saturation value $\langle \epsilon \rangle_{\text{eq}}$ given by (23). The process may be described by introducing a time-dependent “elastic dipole temperature” $T_\sigma(t)$ (analogous to the spin temperature in magnetism) that is distinct from the lattice temperature T_L . We may also make the customary assumption that the number of degrees of freedom in the lattice bath is so large that T_L is, for all practical purposes, independent of time. Then, treating H_h as the interaction term, the density matrix of the system in the Schrödinger representation is given by

$$\rho_S(t) = \frac{\exp(-\beta_\sigma(t) H_\sigma) \exp(-\beta_L H_L)}{\text{Tr} \exp(-\beta_\sigma(t) H_\sigma) \text{Tr} \exp(-\beta_L H_L)} \quad (24)$$

where $\beta_\sigma(t) = 1/k_B T_\sigma(t)$. As $t \rightarrow \infty$ and the system relaxes to its new state of equilibrium, this quantity approaches the asymptotic value β_L , i.e., we have the boundary condition

$$\lim_{t \rightarrow \infty} \beta_\sigma(t) = \beta_L. \quad (25)$$

The measured value of the strain at any time $t > 0$ is

$$\langle \epsilon(t) \rangle = \text{Tr} [\epsilon \rho_S(t)]. \quad (26)$$

Again working to first order in $v_0 \sigma \beta_L$ we have, exactly as in the derivation of (23) above,

$$\langle \epsilon(t) \rangle = \frac{2}{9} v_0 \sigma C (\lambda_1 - \lambda_2)^2 \beta_\sigma(t). \quad (27)$$

The time evolution of the strain is determined, therefore, by $\beta_\sigma(t)$. The latter is found by going over to the interaction representation. An approximate master equation is derived for the density matrix that has the required feature of irreversibility, in order to characterize the process of relaxation.

4. Master equation for the density matrix

The equation $i\hbar d\rho_s/dt = [H, \rho_s]$ is transformed in the interaction representation to

$$i\hbar d\rho_I(t)/dt = [H_h(t), \rho_I(t)]. \quad (28)$$

Here, as usual,

$$H_h(t) = \exp \left[\frac{i}{\hbar} (H_\sigma + H_L)t \right] H_h \exp \left[-\frac{i}{\hbar} (H_\sigma + H_L)t \right], \quad (29)$$

is the hopping Hamiltonian in the interaction representation. (To keep the notation simple, the subscript I is dropped. Retention of the time arguments will indicate operators in the interaction picture). Equation (29) is solved approximately in the standard manner (e.g., see Abragam 1961). We obtain

$$d\rho_I(t)/dt = (i/\hbar) [\rho_I(0), H_h(t)] - (1/\hbar^2) \int_0^t dt' \cdot [H_h(t), [H_h(t-t'), \rho_I(0)]], \quad (30)$$

correct to second order in the hopping term. Next, two further approximations are made, again a standard procedure. First, the term $\rho_I(0)$ in the integral is replaced by $\rho_I(t)$. This makes little difference as long as we work to second order in H_h , i.e., at the level of the correlation function $\langle H_h(t) H_h(t-t') \rangle$. Second, if we are interested in time intervals t that are much larger than the correlation time τ_c characterising $\langle H_h(t) H_h(t-t') \rangle$, it is clearly admissible to extend the upper limit of integration to ∞ without significantly altering the value of the integral. Thus (30) may be replaced by

$$d\rho_I(t)/dt = (i/\hbar) [\rho_I(0), H_h(t)] - (1/\hbar^2) \int_0^\infty dt' \cdot [H_h(t), [H_h(t-t'), \rho_I(t)]]. \quad (31)$$

Equations (24) and (31) will be used to determine the time derivative of $\beta_\sigma(t)$. Equation (27) will then tell us how the strain approaches its saturation value $\langle \epsilon \rangle_{\text{eq}}$.

5. Anelastic relaxations

To find the time derivative of $\beta_\sigma(t)$, let us consider the rate of change of the quantity $\langle A_j(t) \rangle$, where j labels any one of the dipoles. We have in the Schrödinger picture,

$$\begin{aligned} \frac{d}{dt} \langle A_j(t) \rangle &= \frac{d}{dt} \text{Tr} (\rho_s(t) A_j) \\ &= \frac{2}{9} \hbar \omega_\sigma \frac{d}{dt} \beta_\sigma(t), \end{aligned} \quad (32)$$

correct to leading order in $v_0 \sigma \beta_\sigma$; the frequency ω_σ has already been defined in (10).

In the interaction picture, on the other hand, the approximate master equation (31) yields

$$\begin{aligned} \frac{d}{dt} \langle A_j(t) \rangle &= \frac{i}{\hbar} \text{Tr} (A_j [\rho_I(0), H_h(t)]) - \frac{1}{\hbar^2} \int_0^\infty dt' \\ &\quad \text{Tr} (A_j [H_h(0), [H_h(-t'), \rho_s(t)]]]) \end{aligned} \quad (33)$$

after some re-grouping of the final term on the right using the cyclic invariance of the trace. The same property shows that the first term on the right in (33) vanishes, because $[A_j, \rho_I(0)] = 0$. We must now use (24) for $\rho_s(t)$ and simplify the result. Finally, (32) and (33) lead to

$$\frac{d}{dt} \beta_\sigma(t) \approx [\beta_L - \beta_\sigma(t)]/\tau, \quad (34)$$

which expresses the relaxation of $\beta_\sigma(t)$ to the value β_L . The relaxation time τ is given by (see (A.6))

$$1/\tau = (9/2\hbar^2) \int_0^\infty dt' \sum_{i=1}^{N_d} \langle A_i [[A_j, H_h(0)], H_h(-t')] \rangle_{\text{eq}}. \quad (35)$$

Here $\langle \rangle_{\text{eq}}$ stands for the equilibrium expectation value, evaluated using the factored density matrix

$$\tilde{\rho} = \frac{\exp(-\beta_L H_\sigma) \exp(-\beta_L H_L)}{\text{Tr}_d \exp(-\beta_L H_\sigma) \text{Tr}_L \exp(-\beta_L H_L)}, \quad (36)$$

corresponding to the temperature T_L . The subscripts in the traces refer to sums over the states of the dipoles and the lattice respectively. Equation (35) is further reduced in the appendix, and the result is (see (A.19)).

$$\begin{aligned} 1/\tau &= \frac{1}{2} (3 - \tanh \frac{1}{2} \beta_L \hbar \omega_\sigma) S_f(\omega_\sigma) \\ &= \frac{1}{2} \left(3 - \tanh \frac{v_0 \sigma (\lambda_1 - \lambda_2)}{2 k_B T_L} \right) S_f(\omega_\sigma). \end{aligned} \quad (37)$$

Here we have written the elastic dipole—lattice coupling term in H in terms of a quantity with the dimensions of a frequency, according to

$$g \sum_i R_i = \hbar f \sum_i R_i. \quad (38)$$

The important object in (37) is the power spectrum of the operator f , defined as the Fourier transform of its symmetrized correlation function:

$$S_f(\omega) = \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle f(0)f(t) + f(t)f(0) \rangle_{\text{eq}}. \quad (39)$$

Although we have quoted a complicated-looking result in (37), in order to make a certain point in the next section, a further approximation must be made in the above so as to be consistent. Only the leading term in an expansion in powers of $v_0 \sigma \beta_L$ ought to be retained. (It turns out then that this is also equivalent to neglecting the difference between the Fourier transforms of $\langle f(0)f(t) \rangle_{\text{eq}}$ and $\langle f(t)f(0) \rangle_{\text{eq}}$ for frequencies $\omega \leq \omega_\sigma$ — see § 6). We obtain, finally, the relaxation behaviour

$$\langle \epsilon(t) \rangle = \frac{2}{9} v_0 C \sigma (\lambda_1 - \lambda_2)^2 \beta_L [1 - \exp(-t/\tau)], \quad (40)$$

where $1/\tau = (3/2) S_f(\omega_\sigma).$ (41)

Here $S_f(\omega) = 4 \int_0^\infty dt \cos \omega t \langle f(0)f(t) \rangle_{\text{eq}}.$ (42)

The temperature dependence of the relaxation time arises upon computing (in principle!) the expectation value of $f(0)f(t)$ using the density matrix $\exp(-\beta_L H_L)/\text{Tr} \exp(-\beta_L H_L)$. For ready reference, let us observe also that insertion of the typical values $v_0 \approx 10^{-23}$ cm³, $\lambda_1 - \lambda_2 \approx 1$ yields the order of magnitude estimates

$$v_0 \sigma (\lambda_1 - \lambda_2) \beta_L \approx 10^{-7} \sigma \text{ (in dyn cm}^{-2}\text{)}/T_L \text{ (in }^\circ\text{K)} \quad (43)$$

and $\omega_\sigma \text{ (in Hz)} \approx 10^4 \sigma \text{ (in dyn cm}^{-2}\text{)}.$ (44)

If the elastic strain in an experimental situation is of the order of 10^{-5} (e.g., see Robrock *et al* 1977), then $\sigma \approx 10^6$ dyn cm⁻² (using a typical value for the elastic modulus).

Even if T_L is as low as 10^2 K, we have

$$v_0 \sigma (\lambda_1 - \lambda_2) \beta_L \approx 10^{-3}, \quad (45)$$

and

$$\omega_\sigma \approx 10^{10} \text{ Hz.} \quad (46)$$

These values may be regarded as rough *upper* limits for these quantities under normal experimental conditions.

6. Discussion

The interesting physics is contained in the expression for the relaxation time τ . It is convenient to arrange the discussion in the form of a series of comments.

(i) At the very outset, let us make it clear that we have obtained answers *in the classical limit* for a problem that *is* in the classical regime under normal experimental circumstances, albeit by using a quantum mechanical *formalism*. We first list the reasons for using such a formalism, and then explain precisely where the 'classical' approximations have gone in, simultaneously pointing out the modifications necessary to handle a quantum mechanical situation (there does exist such a case).

Our objective in formulating the problem as we have done is three-fold. First, as explained in the Introduction, we are interested in deducing τ as a function of the microscopic parameters involved. Second, the route we have followed, using an approximate master equation for the density matrix that describes relaxation, is a first-principles approach that is in fact easier, and more direct, than a purely classical approach involving the Liouville equation. Third, it is a straightforward matter to go over to the purely classical limit of the formalism. Such a procedure helps us identify precisely the small parameter which measures the accuracy of the limit, and also keep track of the aspects that may need modification when going beyond the classical regime in certain instances.

(ii) Let us now identify the junctures at which a classical limit has been implicitly taken. Considering the defects first, each interstitial atom has been replaced, for the purpose of calculating the anelastic strain, by an elastic dipole which can take on any of a discrete set of orientations. We have found it convenient (for reasons already listed) to associate 'states' with these orientations, and to do quantum mechanics in terms of these states, in writing down the quantum mechanical equation of motion for the density matrix. It should be noted that no *inherently* quantum mechanical features of the dynamics of the original interstitial *atoms* have been brought in. (Even in a purely classical treatment, it would again be quite natural to work in a vector space spanned by the orientation states of the dipoles). In the case of hydrogen interstitials, when quantum tunnelling from one site to another also contributes to the hopping of the defects, such features would of course have to be considered too.

Further, to point out what is perhaps obvious, we have used *classical* or Maxwell-Boltzmann *statistics* for the collection of elastic dipoles. This is evident from the direct product states we have used for the system of dipoles, *without* any symmetrization or anti-symmetrization. The use of classical statistics is of course appropriate in view of the low interstitial concentrations involved (and has nothing to do with the absence of defect-defect interactions!). At high defect concentrations, when the underlying defect atoms form a degenerate gas in the host lattice, it may be necessary to use the appropriate quantum statistics as well, for light interstitials.

Finally, let us turn to the treatment of the 'larger' system (the lattice) that absorbs the energy released by the system of dipoles during the relaxation. It is quite evident from (A.14), (A.15) and (37) that the result given in (41) and (42) is simply a high temperature approximation. The small parameter in our problem is $\beta_L \hbar \omega_\sigma = \nu_0 \sigma (\lambda_1 - \lambda_2) / k_B T_L$. The numerator is just the energy released by a dipole in a single reorientation from a transverse direction to the direction of the tensile stress. When T_L is sufficiently large, this ratio is much smaller than unity, and our simplifications

hold good. Now the $\tanh(\beta_L \hbar \omega_\sigma / 2)$ term in (37) actually arises from the commutator of $f(0)$ and $f(t)$ (see (A.15)). One might therefore jump to the conclusion that the high temperature limit is equivalent to treating the lattice classically, with $f(t)$ a c -number. This is not so. The point is illustrated most simply by writing the spectral theorem of (A.15) in the form

$$\begin{aligned} & \exp(\beta_L \hbar \omega) \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle f(0) f(t) \rangle_{\text{eq}} \\ &= \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle f(t) f(0) \rangle_{\text{eq}}, \end{aligned} \quad (47)$$

valid for all real values of ω . We are merely saying that when $\omega = \omega_\sigma$ such that $\beta_L \hbar \omega_\sigma \ll 1$, the two Fourier transforms become approximately equal to each other and the contribution (to $1/\tau$) from their difference becomes negligible. Obviously, the same statement is true for all ω in the range $0 \leq \omega \leq \omega_\sigma$. This clearly does not imply the equality of the two Fourier transforms at *all* values of ω , so that our approximation does *not* amount to neglecting $\langle [f(0), f(t)] \rangle_{\text{eq}}$, much less $[f(0), f(t)]$ itself. This is as it should be, for there certainly occur cases when it is necessary to treat $f(t)$ as a quantum mechanical operator in the space of lattice states. For example, if the modelling is done via phonon operators, the correct quantum statistics for the phonons must be used in evaluating the contributions from the direct (one-phonon) process, the Raman process, and so on, each with its characteristic temperature dependence. For hydrogen interstitials, such a treatment is necessary (Stoneham 1972). It can be shown, for instance, that the hopping rate of the interstitials tends to a T_L^7 dependence at very low temperatures, in contrast to the standard Arrhenius type of dependence.

(iii) The case of a very light interstitial such as H , which we have referred to above, is a very interesting one in view of the possible contribution to the relaxation from quantum mechanical tunnelling that should become observable at very low temperatures (Heller 1961; Gibala 1967; Lord 1967; however, also see Moser *et al* 1977). In addition to the modifications noted above, another fact must be taken into account. What actually occurs in this instance is a complicated interplay of classical and quantum effects. In addition to thermally activated jumps from one site to another, the interstitials can tunnel through neighbouring potential barriers that are themselves lowered randomly by thermal fluctuations, leading to an unusual sort of diffusion process (Flynn and Stoneham 1970; Stoneham 1972; Kehr 1976). Recently, a *time-dependent* description of quantum tunnelling has been given by Yasue (1978) based on the concept of stochastic quantization (Nelson 1966). An attempt is being made to apply this description to the calculation of the relevant power spectrum that features in the relaxation time for the case of very light interstitial atoms, when tunnelling contributes significantly.

(iv) With these general remarks out of the way, we may turn to the results expressed in (40)–(42). The relaxation occurs because of the time dependence of the defect hopping term, $f(t)$. (Without this dependence, we should simply find $\tau \rightarrow \infty$). This inherently irreversible behaviour is a consequence of the coupling of a very large number of degrees of freedom with those of the defect 'system'. The difficult problem, of course, is the evaluation of the correlation function $\langle f(0) f(t) \rangle_{\text{eq}}$,

where f is an operator acting on the states of the lattice. We may refer to Redfield (1965), Berne and Harp (1970), and Forster (1975) for pertinent remarks in this connection. It is clear that the very large number of degrees of freedom involved in the lattice bath makes it expedient to use some sort of stochastic technique for the determination of the correlation function. It is convenient, from a practical point of view, to regard the hopping term in the Hamiltonian as a random perturbation of the (elastic dipole) system. In the so-called 'semiclassical approximation' (Abragam 1961, Ch. 8), one simply assumes that $\beta_L \rightarrow 0$ in the calculation of the relaxation time. The lattice density matrix reduces to $1/L$, where L is the (very large) number of degrees of freedom of the lattice. We then have $\langle f(0)f(t) \rangle_{\text{eq}} \rightarrow \overline{f(0)f(t)}$, the bar standing for the statistical average of the corresponding random function of time. However, the temperature dependence of the relaxation time is lost in this approximation. In order to retain this physically significant temperature dependence, one may regard the lattice as a classical heat bath at a finite temperature T_L , and $f(t)$ as a stationary random variable, and appropriately model the temperature dependence of the ensemble to be averaged over. The relaxation time is given by (42), where $S_f(\omega_\sigma)$ corresponds precisely to the customary definition of the power spectrum of the random variable f , evaluated at the frequency ω_σ . We have already seen that this frequency (in Hertz) is typically of the order of $10^4\sigma$, where σ is the applied stress expressed in dyne cm^{-2} .

(v) The simplest model for $f(t)$ corresponds to assuming that it is purely random, i.e., a white noise. Its power spectrum is then a constant. It is more plausible, physically, to assume that the random process $f(t)$ which drives the fluctuations in the elastic dipole orientations is a stationary process that is Markovian. For convenience, one assumes also that it is a Gaussian process. Therefore its autocorrelation is of the form (Doob 1942).

$$\overline{f(0)f(t)} = \overline{f^2} \exp(-t/\tau_c) \equiv \omega_h^2 \exp(-t/\tau_c) \quad (48)$$

where τ_c is the correlation time, and ω_h is the *effective hopping parameter* defined as the rms value of the hopping energy expressed in frequency units. Equations (41) and (42) then yield

$$1/\tau = 6\omega_h^2 \tau_c / (1 + \omega_\sigma^2 \tau_c^2). \quad (49)$$

In phenomenological rate theory (Nowick and Berry 1972), one simply assumes that $1/\tau$ is directly proportional to the 'dipole re-orientation frequency', and this in turn is assumed to have an Arrhenius form of temperature dependence. We find that $1/\tau$ actually depends on two microscopic parameters, ω_h and τ_c , that relate to the coupling term $f(t)$ inducing the re-orientations.

(vi) Before we discuss the temperature dependence of τ , let us point out the similarities and differences between the present situation and magnetic relaxation. In the latter case, a common coupling mechanism that leads to the relaxation is the dipole-dipole interaction between the magnetic moments of the system, which causes the transfer of Zeeman energy to the lattice. A form similar to that of (49) is obtained for the relaxation time, namely,

$$1/\tau \sim h_d^2 \tau_c / (1 + \omega_B^2 \tau_c^2). \quad (50)$$

Here h_d stands for the spatial part of the dipole-dipole interaction suitably averaged over the lattice, and τ_c is the corresponding correlation time. The frequency ω_B is proportional to the external magnetic field B . It is customary to assume an Arrhenius form of temperature dependence for τ_c and to regard h_d as approximately T -independent. Then, as is well known (Slichter 1963), a plot of $\ln \tau$ versus $1/T$ shows an initial decrease to a minimum given by $\omega_B \tau_c = 1$, then a rise (in the region $\omega_B \tau_c > 1$). Such a variation is borne out by experiment, as is the dependence on the applied field B via ω_B . In the case of anelastic relaxation, on the other hand, the data from a variety of experiments (elastic after-effect measurements, internal friction, direct measurements of the interstitial diffusion coefficient, etc.) show that $\ln \tau$ increases linearly with $1/T$ over a wide range of temperature (Nowick and Berry 1972). Nor is there any evidence of a dependence on the applied stress σ (as is obvious from the preceding statement itself). We explain these facts as follows. While (49) and (50) are formally similar in structure, the physical origins of ω_h and h_d are quite different. The dipole-dipole coupling persists even at very low temperatures, and it is perhaps reasonable to ignore its possible T -dependence. In contrast, the hopping energy $\hbar\omega_h$ in our problem may be expected to be strongly temperature-dependent, since the hopping occurs when the interstitial atom overcomes a potential barrier. It is therefore plausible to model ω_h according to

$$\omega_h = \omega_\infty \exp(-Q_h/k_B T), \quad (51)$$

and also retain the standard assumption

$$\tau_c = \tau_\infty \exp(Q_c/k_B T), \quad (52)$$

where Q_h and Q_c are the corresponding activation energies. (It is very likely, further, that $Q_h \approx Q_c$, since they refer to the same mechanism). Using these functions of T , we find from (49)

$$\ln \tau \approx \ln(1/6\omega_\infty^2 \tau_\infty) + Q/k_B T \quad (\omega_\sigma \tau_c \ll 1), \quad (53)$$

where $Q = (2Q_h - Q_c)$ is the effective activation energy; while

$$\ln \tau \approx \ln(\omega_\sigma^2 \tau_\infty / 6\omega_\infty^2) + Q'/k_B T \quad (\omega_\sigma \tau_c \gg 1), \quad (54)$$

where $Q' = (2Q_h + Q_c)$. Thus $\ln \tau$ is always an increasing function of $1/T$. An increase in slope is expected around $\omega_\sigma \tau_c \approx 1$, beyond which points corresponding to different values of the applied stress should lie on different curves because of the dependence on ω_σ in (54).

However, as we have already mentioned, the data over a wide range of T (roughly 50°K to 700°K) for anelastic relaxation times agree well with a single component Arrhenius fit that is, moreover, independent of σ (e.g., see Powers and Doyle 1959; Lord and Beshers 1966, Farraro and McLellan 1978, Robrock *et al* 1977). The reason for this becomes evident on estimating the magnitude of $\omega_\sigma \tau_c$ in practical situations. The correlation or 'memory' time τ_c cannot be very much larger than

the inverse of the highest phonon frequencies in the host material, i.e., about 10^{-13} sec. Even if $\tau_c \approx 10^{-12}$ sec, $\omega_\sigma \tau_c \approx 10^{-2}$ (see (46)), and $(\omega_\sigma \tau_c)^2$ is negligible compared to unity. Thus one is generally restricted to the region where (53) is appropriate. (We note parenthetically that this is also the result one would obtain if (48) is replaced by the white noise assumption for $f(t)$: in this case $\omega_h^2 \rightarrow \infty$ and $\tau_c \rightarrow 0$ such that $\omega_h^2 \tau_c$ is a finite number Γ , and $f(0)f(t) = \Gamma \delta(t)$). In principle, this restriction precludes a determination of the two parameters ω_h and τ_c separately from a measurement of τ , unlike the case of magnetic relaxation. Experiments yield a characteristic value of 5×10^{-15} sec for the pre-factor in τ , so that we have $\omega_\infty^2 \tau_\infty \approx 10^{-14}$ sec. It is also found that $Q \approx 1$ eV. One may be able to detect the onset of the second region (54) by working at lower temperatures and higher values of σ , retaining however the condition $v_0 \sigma \beta_L \ll 1$. However, there is a further complication in doing so, that is not present in the study of magnetic relaxation. At stress levels of the order of 10^8 dyn cm^{-2} , departures from anelastic behaviour itself are likely, as the yield stress is approached.

(vii) There is a parenthetical remark that we should like to make regarding the appearance of the applied stress σ in the expression for τ given in (41) or in (49). Now, from experimental considerations, it has been pointed out (Robrock 1974) that anelastic relaxation is very conveniently studied by using the elastic after-effect technique (Nowick and Berry 1972; for recent experiments, see for instance Spiric *et al* 1977; Robrock *et al* 1977). If the stress-strain relationship is rigorously a linear one, the elastic after-effect function is of course determined by the creep function itself. It might appear that we have lost this possibility in introducing a non-linearity into the problem by means of the stress dependence of the relaxation time (although, as we have argued, this is not directly accessible to detection). However, we should like to emphasize that the crucial and central property that characterizes anelastic behaviour is *full recoverability*, i.e., a unique equilibrium relationship between stress and strain. (This of course implies that the equilibrium is attained for any constant stress, after a sufficiently long interval, in marked contrast to viscoelastic behaviour or more complicated modes of plastic deformation.) Linearity is merely put in as a convenience. Our theory is easily extended to show that the strain in an elastic after-effect experiment will relax to zero from its *initial* equilibrium value under a constant stress σ , once σ is switched off at $t = 0$, according to

$$\langle \epsilon(t) \rangle = \langle \epsilon \rangle_{\text{eq}} \exp(-t/\tau). \quad (55)$$

Here $\langle \epsilon \rangle_{\text{eq}}$ is precisely the saturation value given by (23) and τ is again the same relaxation time as in the creep function, namely, the expression given in (41).

(viii) In paper I, the results of the application of linear response theory were verified by developing an alternate formalism to study the microscopic strain and stress fluctuations. This was based on a Langevin-like stochastic equation for the fluctuating strain driven by a random internal stress caused by defect motion. Theorems relating the relaxation time to the power spectra of the fluctuating stress and strain were developed. It is possible to make a connection between those relations and the results of this paper. In addition, of course, our present formalism has side-stepped the question of obtaining a quantum mechanical

generalization of the Langevin equation in the present context, and has also enabled us to deduce an expression for τ in terms of somewhat more basic parameters. In this sense, we now have a more generally applicable theory of anelastic relaxation.

(ix) Finally, a remark on the strain response to a time-dependent applied stress: the entire theory can be modified to evaluate the complex compliance $J(\omega)$ of the system, even if we do not wish to restrict ourselves to linear response theory and directly use the relaxation-response relationship between $J(\omega)$ and the creep function. An explicit demonstration of this statement is unnecessary, since the time-dependence of the relaxation (i.e., the creep function) actually contains complete information on the anelastic behaviour of the material under study.

Acknowledgement

We should like to thank Dr B Purniah for acquainting us with some of the experimental references.

Appendix

We outline here the steps which lead to (40) and (41) for the relaxation of $\langle \epsilon(t) \rangle$ to its saturation value, starting with (32) and (33) together with (24) for the density matrix $\rho_s(t)$.

Equation (33) yields

$$\begin{aligned} \frac{d}{dt} \langle A_j(t) \rangle &= - (1/\hbar^2) \int_0^\infty dt' \text{Tr} \{ A_j [H_h(0), [H_h(-t'), \rho_s(t)]] \} \\ &= - (1/\hbar^2) \int_0^\infty dt' \text{Tr} \{ \rho_s(t) [[A_j, H_h(0)], H_h(-t')] \}, \end{aligned} \quad (\text{A.1})$$

on using the cyclic invariance of the trace. Now (24) for $\rho_s(t)$ can be written as

$$\rho_s(t) \approx \tilde{\rho} [I - (\beta_\sigma(t) - \beta_L) H_\sigma], \quad (\text{A.2})$$

where

$$\tilde{\rho} = \frac{\exp(-\beta_L H_\sigma) \exp(-\beta_L H_L)}{\text{Tr}_d \exp(-\beta_L H_\sigma) \text{Tr}_L \exp(-\beta_L H_L)}, \quad (\text{A.3})$$

and Tr_d , Tr_L , refer respectively to traces over the orientation states of the dipoles and the lattice states. In (A.2), we have retained only terms upto first order in the small quantity $(\beta_\sigma(t) - \beta_L) v_0 \sigma (\lambda_1 - \lambda_2)$. The term involving I in (A.2) merely gives a constant when substituted in (A.1), and may be dropped as the boundary condition on $\beta_\sigma(t)$ is $\beta_\sigma(\infty) = \beta_L$.

We find then

$$\frac{d}{dt} \langle A_j(t) \rangle = (1/\hbar^2)(\beta_\sigma(t) - \beta_L) \int_0^\infty dt' \text{Tr} \{ \tilde{\rho} H_\sigma [[A_j, H_h(0)], H_h(-t')] \}. \quad (\text{A.4})$$

Comparing this with (32), we immediately obtain

$$\frac{d}{dt} \beta_\sigma(t) = (\beta_L - \beta_\sigma(t))/\tau, \quad (\text{A.5})$$

where

$$1/\tau = (9/2\hbar^2) \int_0^\infty dt' \sum_{i=1}^{N_d} \langle A_i [[A_j, H_h(0)], H_h(-t')] \rangle_{\text{eq}}. \quad (\text{A.6})$$

This is the formal expression for the relaxation time, quoted in (35) in the text. The symbol $\langle \rangle_{\text{eq}}$ stands for the equilibrium expectation value, evaluated using the factored density matrix $\tilde{\rho}$ corresponding to the temperature T_L .

We may now begin the explicit evaluation of $(1/\tau)$ for the problem at hand. We find

$$[A_j, H_h(0)] = g(0) M_{1j} \quad (\text{A.7})$$

and

$$H_h(-t') = g(-t') \sum_{i=1}^{N_d} (iM_{1i} \sin \omega_\sigma t' + M_{2i} \cos \omega_\sigma t' + M_{3i}), \quad (\text{A.8})$$

where the operators M_{qi} ($q=1, 2, 3$) have the usual direct product representations. The respective matrices that act in the space of the i th dipole are

$$m_1 = \begin{pmatrix} 0 & 1 & 1 \\ -1 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad m_2 = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad m_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}. \quad (\text{A.9})$$

The double commutator required in (A.6) may now be calculated. However, we need only the trace of the product of this operator with a *diagonal* operator, namely, $\exp(-\beta_L H_\sigma) \Sigma A_i$. If (m) is a (3×3) matrix with zeros on the diagonal and (n) is a diagonal (3×3) matrix, (mn) and (nm) again have zeros on the diagonal, and do not contribute to the final trace. This fact simplifies the algebra considerably. We finally obtain

$$\begin{aligned} (1/\tau) = & (9/2\hbar^2) \langle \sum_i A_i L_j \rangle_{\text{eq}} \int_0^\infty dt (3 \langle \{g(0), g(-t)\} \rangle_{\text{eq}} \cos \omega_\sigma t \\ & - i \langle [g(0), g(-t)] \rangle_{\text{eq}} \sin \omega_\sigma t) - (9/2\hbar^2) \langle \sum_i A_i \rangle_{\text{eq}} \times \\ & \int_0^\infty dt (\langle \{g(0), g(-t)\} \rangle_{\text{eq}} \cos \omega_\sigma t + i \langle [g(0), g(-t)] \rangle_{\text{eq}} \sin \omega_\sigma t). \end{aligned} \quad (\text{A.10})$$

Here $\{g(0), g(-t)\}$ stands for the anti-commutator, and

$$L_j = \mathbf{1}_1 \otimes \dots \otimes \mathbf{1}_{j-1} \otimes (I)_j \otimes \mathbf{1}_{j+1} \dots \otimes \mathbf{1}_{N_d}, \quad (\text{A.11})$$

$$I = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (\text{A.12})$$

The equilibrium expectation values indicated have the obvious meaning, i.e., for A_i, L_j , etc., the density matrix is $\exp(-\beta_L H_\sigma) / \text{Tr} \exp(-\beta_L H_\sigma)$; while for the operators $g(0)$ and $g(t)$ it is $\exp(-\beta_L H_L) / \text{Tr} \exp(-\beta_L H_L)$.

The possible quantum mechanical nature of the operator g has been retained in deriving (A.10), although the lattice may have a *large* number of degrees of freedom. Since only equilibrium expectation values occur in the result, further simplification is possible on using the stationarity property

$$\langle g(0)g(-t) \rangle_{\text{eq}} = \langle g(t)g(0) \rangle_{\text{eq}}. \quad (\text{A.13})$$

The expectation values of the anti-commutator and commutator are therefore even and odd functions of t respectively. Equation (A.10) may thus be written in terms of the Fourier transforms of these combinations. The power spectrum of g is defined as the Fourier transform of the 'symmetrized correlation', i.e.,

$$S_g(\omega) = \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle \{g(0), g(t)\} \rangle_{\text{eq}}. \quad (\text{A.14})$$

As is well known, the Fourier transform of the anti-symmetrized correlation can be related to $S_g(\omega)$ by a spectral theorem (which subsequently leads to the fluctuation-dissipation relationship in linear response theory!):

$$\int_{-\infty}^{\infty} dt \exp(i\omega t) \langle [g(0), g(t)] \rangle_{\text{eq}} = -S_g(\omega) \tanh(\frac{1}{2}\beta_L \hbar \omega). \quad (\text{A.15})$$

Our result for the relaxation time takes the form

$$\begin{aligned} 1/\tau = & (9/4\hbar^2) S_g(\omega_\sigma) [(3 - \tanh \frac{1}{2}\beta_L \hbar \omega_\sigma) \langle \Sigma_i A_i L_j \rangle_{\text{eq}} \\ & - (1 + \tanh \frac{1}{2}\beta_L \hbar \omega_\sigma) \langle \Sigma_i A_i \rangle_{\text{eq}}]. \end{aligned} \quad (\text{A.16})$$

Now we have worked throughout to first order in the quantity $v_0 \sigma \beta_L$. Consistency therefore demands that $\langle A_i \rangle_{\text{eq}}$ and $\langle A_i L_j \rangle_{\text{eq}}$ be determined using only the leading term in a corresponding expansion of the density matrix $\tilde{\rho}$, as is clear from an inspection of (A.2) and (A.5). In other words, we must write

$$\exp(-\beta_L H_\sigma) / \text{Tr} \exp(-\beta_L H_\sigma) \approx I / \text{Tr} I, \quad (\text{A.17})$$

as far as (A.16) is concerned. (We do *not* imply by this a similar approximation for the lattice part of the density matrix $\tilde{\rho}$!). Since A_i is traceless, the second term in

square brackets in (A.16) vanishes. We have also $\text{Tr}(A_j L_j) = 2/9$. It is convenient (see, e.g., Abragam 1961, Ch. 9) to write the elastic dipole-lattice coupling term in the Hamiltonian in terms of a quantity with the dimensions of a frequency, according to

$$g \Sigma_i R_i \equiv \hbar f \Sigma_i R_i. \quad (\text{A.18})$$

The relaxation time is therefore given by

$$1/\tau = \frac{1}{2} (3 - \tanh \frac{1}{2} \beta_L \hbar \omega_\sigma) S_f(\omega_\sigma), \quad (\text{A.19})$$

where
$$S_f(\omega) = \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle \{f(0), f(t)\} \rangle_{\text{eq}}. \quad (\text{A.20})$$

This is the answer written down in (37). Recalling that we must work to leading order in $v_0 \sigma \beta_L$, this further simplifies to

$$1/\tau = (3/2) S_f(\omega_\sigma), \quad (\text{A.21})$$

where (as explained in the text)

$$S_f(\omega) = 4 \int_0^{\infty} dt \cos \omega t \langle f(0) f(t) \rangle_{\text{eq}} \quad (\text{A.22})$$

is the power spectrum of the c -number function $f(t)$.

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