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Theory of the Gorsky effect for low interstitial concentrations

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Abstract. The formalism of the preceding paper is applied to work out the theory of the Gorsky effect, or anelastic relaxation due to the long-range diffusion of interstitials in a host lattice, for non-interacting (low-concentration) interstitials (e.g., H in Nb). It is shown how linear response theory (LRT) provides a number of advantages that simplify the solution of the problem and permit the handling of complications due to specimen geometry and stress inhomogeneity. The multiple-relaxation time creep function of Alefeld *et al* is first re-derived. Next, the dynamic responseand the short-time behaviour of the creep function are deduced exactly, and the $\omega^{-1/2}$ fall-off of the internal friction at high frequencies is exhibited. Finally, it is pointed out that the true asymptotic behaviour of the dynamic response must be found by going beyond the diffusion equation model. A two-state random walk analysis is used to predict a cross-over to a true ω^{-1} asymptotic behaviour, and the physical reasons for this phenomenon are elucidated.

Keywords. Gorsky effect; elastic diffusion relaxation; hydrogen in metals; internal friction; random walk.

1. Introduction

In the preceding paper (Balakrishnan 1978; referred to as I hereafter), we have developed a general analysis of the phenomenon of anelasticity based on linear response theory (LRT). The formalism has been worked out in further detail in the case of anelastic behaviour caused by the stress-modulated kinetics of the elastic dipoles associated with point defects. In the first paper of this series (Balakrishnan *et al* 1978; referred to as BDV here and in I), we have already tested the LRT method in a simplified situation: namely, the re-orientation relaxation of $\langle 100 \rangle$ tetrahedral elastic dipoles under a homogeneous uniaxial stress in the [100] direction (a special case of the Snoek effect). In the present paper, we concentrate on the diffusion relaxation due to interstitial atoms that is induced by a dilation gradient in the material.

This phenomenon, called the Gorsky effect (Gorsky 1935; Zener 1948; Schaumann *et al* 1968), has only recently become the focus of a considerable amount of experimental interest, with the advent of the physics of hydrogen in metals (see Völkl and Alefeld 1976 and references therein). In a beautiful paper, Alefeld *et al* (1970) have given a theory of this effect (also called elastic diffusion relaxation). One of the purposes of the present paper is to show how the results required follow very easily from LRT. To the other advantages of our approach (already expounded in BDV), we may add the following important points. We do not need any *ad hoc* ' linearization ' of the diffusion equation, as in other approaches. Further, since it is the *equilibrium* (zero applied stress) autocorrelation that controls the linear response of the system (the fluctuation-dissipation relationship!), all the essential dynamics pertains to the stress-free situation. This means that the applied stress can have any spatial and temporal dependence, without increasing the complexity of the problem in too serious a manner. Similarly, the application of the theory to more complicated specimen geometries does not pose as much of a problem as in other approaches: in the latter, the boundary condition complications are compounded by the presence of the inhomogeneous (external stress) term in the diffusion equation, as will become clear subsequently. Indeed, our use of LRT enables us to get away from the diffusion equation model altogether if need be, and to feed in directly the results of a random walk analysis of the diffusion of the defects, as in the final chapter.

An outline of this paper is as follows. After deriving an (already known) expression for the creep function corresponding to the Gorsky effect in § 2.1. and 2.2, we turn to the dynamic response and the short-time behaviour of the creep function in § 2.3. A Laplace transform method is used to deduce the above quantities exactly (eqs (25) and (19)). Appendices A and B contain some of the mathematical details. We obtain also the $\omega^{-1/2}$ fall-off of the internal friction in the diffusion equation model, in contrast to the ω^{-1} behaviour corresponding to the Debye spectrum characteristic of a single relaxation time. As already pointed out (Doremus 1971), experimental data tend to confirm the $\omega^{-1/2}$ behaviour. The physical reason for this circumstance is explained. Finally, in § 3, we point out that the true asymptotic behaviour of the dynamic response (or the internal friction) must be found by going beyond the diffusion equation model. Drawing upon the results of a microscopic, two-state random walk model of the jump diffusion of interstitials (Balakrishnan and Venkataraman 1975, 1978), we deduce the short-time behaviour of the mean square displacement of an interstitial atom; a stratagem is then presented that enables the true asymptotic behaviour of the internal friction to be predicted (eq. (42)). This turns out to involve a crossover back to a ω^{-1} power law, the deviations from the $\omega^{-1/2}$ fall-off being expected to be observable in high-frequency ultrasonic attenuation measurements. Certain pertinent details of the random walk model are summarized in appendix C.

Finally, we repeat that the purpose of our exposition of the theory of the Gorsky effect in this paper is mainly to draw attention to the power of our LRT-cum-stochastic approach to defect kinetics in general and mechanical response in particular. Partly for the sake of brevity, we have not presented here the version of theory that is appropriate to the more interesting aspects of the effect that manifest themselves at higher interstitial concentrations. These features of current experimental interest include exotic isotope effects for H, D or T in various metals (see, e.g., Richter *et al* 1977), unconventional temperature dependence of the diffusion coefficient, sample-shape dependence of the stability curves (spinodals) of hydrogen-metal systems, etc., all of which are neatly summarized in Völkl and Alefeld (1976). Extensions of our theory to cover some of the as-yet-open aspects of these questions (for instance, a ‘ non-local ’ theory taking into consideration coherence stresses in the host metal, caused by the long-ranged nature of the H-H elastic interaction) will be presented elsewhere.

In what follows, we use the notation introduced in I throughout. Equations occurring in paper I will be referred to as (I. 1), etc.

2. Gorsky relaxation due to interstitial hydrogen

2.1. *Interstitial H in bcc metals*

We shall now work out the theory of elastic diffusion relaxation due to interstitial atoms (specifically H; see below) in bcc metals such as Fe, Nb, V, etc. Although, as in the case of the Snoek effect, it is once again the jump of impurity atoms from one interstitial site to a neighbouring one that leads to the long-range diffusion of these defects, there are at least two distinct time scales in the problem. The first is the reciprocal of the mean atomic jump frequency ν itself, and this controls the re-orientation or Snoek effect. On the other hand, the long-range diffusion is characterised by a time scale $\sim L^2/D$ where L is the linear dimension of the specimen along which diffusion takes place and D is the interstitial diffusion constant. Since $D \sim a^2\nu$ where a is the atomic jump distance, the ratio of the diffusion relaxation time to the re-orientational relaxation time is a very large number, of the order of $(L/a)^2$ (Alefeld *et al* 1970). To bring the Gorsky effect within the reach of experimental feasibility, it is therefore necessary to use very thin samples (small L) and, more important, interstitials with high mobility (e.g., hydrogen). Both hydrogen and deuterium molecules dissociate and are present as H or D in interstitial sites, with extraordinarily high mobilities. It is these systems that experiments have concentrated on (Schaumann *et al* 1968, 1970; Völkl *et al* 1970, 1971; Cantelli *et al* 1970; see also Alefeld 1975 and references therein; Richter *et al* 1977). In order to be specific, we shall restrict our attention wherever necessary to bcc host metals (e.g., Nb), considerable experimental interest being attached to systems such as H or D in Nb. The theory to be developed is of course quite general in its applicability.

Interstitial hydrogen in bcc niobium occupies tetrahedral sites (Somenkov *et al* 1968; Wert *et al* 1970; Wagner and Horner 1974). There are twelve sites (four each of types 1, 2 and 3) per cubic elementary cell containing two host atoms. Figure 1 shows these sites, labelled by the cube axis that site distinguishes. Each interstitial defect forms a $\langle 100\rangle$ tetragonal elastic dipole. The $\boldsymbol{\lambda}$ tensor is diagonal, with components λ_1, λ_2, $\lambda_3=\lambda_2$, and principal axes along the cube axes themselves. The direction along which the components is λ_1 can be used to label the orientation, and these labels are the same as those of figure 1 (thus the number of distinct orientations $r=3$). The components of the deviatoric (traceless) part of the $\boldsymbol{\lambda}$ tensor are, in this case,

$$\hat{\lambda}_{ij}^{(n)} = \begin{cases} (2/3)\,(\lambda_1 - \lambda_2)\,\delta_{ij} & (n = i), \\ -\,(1/3)\,(\lambda_1 - \lambda_2)\,\delta_{ij} & (n \neq i), \end{cases} \tag{1}$$

where n is the orientation index as in I (in the present case, $n=1, 2, 3$). We also use the notation

$$\lambda = (1/3)\,\mathrm{Tr}\,\boldsymbol{\lambda}^{(n)} = (1/3)\,(\lambda_1 + 2\,\lambda_2). \tag{2}$$

One can now proceed to simplify the general results of I to the case at hand. The deviatoric part of the strain in (I. 21), produced by the re-orientation of the dipoles and modulated by the diffusion in the presence of the stress gradient, is proportional to the square of the anisotropy factor, namely, $(\lambda_1-\lambda_2)^2$. This part describes the

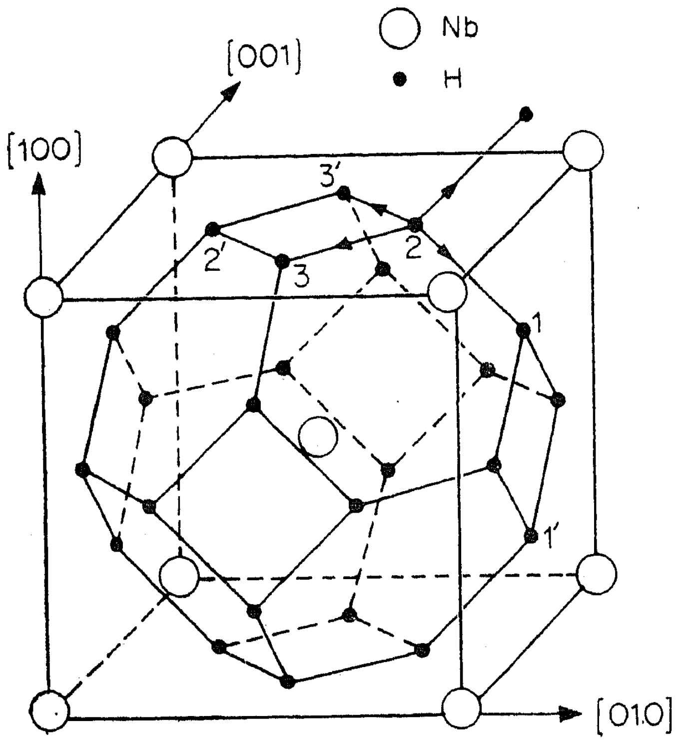

Figure 1. Tetrahedral interstitial lattice for H in bcc Nb, formed by six non-equivalent sites per unit cell. These are situated at the maximum distance from all adjacent bcc sites. The tetrahedral sites are labelled 1, 1′, 2, 2′, 3, 3′, where the numerals refer also the orientation of the corresponding tetrahedral elastic dipole. The arrows indicate possible *nn* jumps from a typical site, the jump distance being $a/2\sqrt{2}$.

Snoek effect due to the interstitial hydrogen, and the theory follows essentially along the lines of BDV. More interesting in the present context is the dilatory part of the strain, proportional to the square of the trace of the dipole tensor, occasioned by the stress gradient. We shall devote our attention to this part of the strain response, as the theoretical techniques required to handle it differ somewhat from those employed in BDV for the orientational relaxation. Besides, it is an experimental fact* (Bucholz *et al* 1973; Alefeld 1975; Pick and Bausch 1976) that for hydrogen in metals such as Nb, V or Ta, the strain field around the defect departs from cubic symmetry only to the extent of 2%. It is therefore quite justifiable, as far as H in Nb is concerned, to concentrate on the diffusion relaxation alone—*both* because the re-orientational effect is very much smaller than is usually the case with other interstitials, *and* because the diffusion effect is extraordinarily large (so that it is experimentally observable) owing to the high mobility of H.

2.2. *Anelastic creep due to H diffusion*

The strain response to a time-independent stress applied from $t=0$ onwards will be

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*Pick and Bausch (1976) find the following values for the principal components of the force dipole tensor **P** that is related to our elastic dipole tensor λ, the latter being essentially the compliance (of the host metal) times the former. The component A (related to λ_1)$=2\cdot88$ eV, while the component B (related to λ_2)$=2\cdot84$ eV, assuming that the nearest neighbour H-H interaction is attractive. This leads to a value $0\cdot01$ for $3(A-B)/(A+2B)$, a measure of the 'anisotropy'. Even if the above interaction is repulsive, this measure is only $\approx 0\cdot05$ ($\ll 1$).

analysed first. The formal expression for this quantity is given by (I.21). Dropping the deviatoric part of the strain for reasons already explained, we have

$$\langle \epsilon_{ij}(\mathbf{R}, t)\rangle = \beta\, C\, v_0\, \lambda^2\, \delta_{ij} \int_V d\mathbf{R}'\, \mathrm{Tr}\, \sigma(\mathbf{R}') \left(\mathbf{R}' \middle| 1 - P_d^{\mathrm{eq}}(t) \middle| \mathbf{R}\right). \tag{3}$$

For ready reference, we explain the notation once again. $\beta = 1/k_B T$, v_0 is the volume per atom of the sample under study, C is the molefraction of interstitials, and σ is the applied stress field. $|\,\mathbf{R})$ refers to a stochastic state labelled by the position vector $\mathbf{R}$. The matrix element $\left(\mathbf{R}' \middle| P_d^{\mathrm{eq}}(t) \middle| \mathbf{R}\right)$ represents the conditional probability for an interstitial to evolve from the state $|\,\mathbf{R}')$ at $t = 0$ to the state $|\,\mathbf{R})$ at time t; it is thus closely related to the probability for diffusion from one point to the other. The experimental specimens generally have either a slab geometry or a cylindrical one, and we consider the former case for the sake of definiteness: the stress field is applied to a thin foil that may be regarded as a rectangular parallelopiped of thickness L (in the x-direction) that is much smaller than its length and breadth (taken to lie in the y and z directions).* We have in mind a bending of the specimen that leads to a stress field of the form (e.g., see Alefeld *et al* 1970).

$$\sigma_{kl}(\mathbf{R}) = \sigma_{kl}(x) = \sigma^0_{kl}\,(1 - (2x/L)), \quad (0 \leqslant x \leqslant L), \tag{4}$$

which is dependent on the x-co-ordinate alone, and σ^0 is the notation we use for the stress on the face $x = 0$. The stress is zero at the neutral axis (or plane) $x = \frac{1}{2}L$, as required, and decreases linearly with x to the value $-\sigma^0$ at the opposite face, $x = L$. While this is a convenient special case that applies in certain experimental situations, we emphasize strongly that our formalism (based on LRT) is eminently suited to handle arbitrarily varying stress fields as well: the stress occurs *outside* the matrix element in (3), and the time evolution is determined by $P_d^{\mathrm{eq}}(t)$, which refers to the *unstressed* specimen, as already stated in the Introduction.

The central problem, then, is the evaluation of the matrix element $\left(\mathbf{R}' \middle| P_d^{\mathrm{eq}}(t) \middle| \mathbf{R}\right)$. In the simplest model, this conditional probability obeys the partial differential (or diffusion) equation (Chandrasekar 1943)

$$\partial f(\mathbf{R}, t)/\partial t = D \nabla^2 f(\mathbf{R}, t), \tag{5}$$

subject to the initial condition

$$f(\mathbf{R}, 0) = \delta(\mathbf{R} - \mathbf{R}') = \delta(x - x')\,\delta(y - y')\,\delta(z - z'), \tag{6}$$

where D is the (interstitial) diffusion constant. According to a well known theorem (see, e.g., Crank 1956), the solutions to the equation are then expressible as products of functions of (x, t), (y, t) and (z, t). Since $\sigma(\mathbf{R})$ has no y or z dependence,

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*For example, Cantelli *et al* (1970) studied the case of H in V using a foil 2×10^{-3} cm thick, 1·2 cm wide and 5·0 cm long. The specimen was clamped at one end and the damping of the flexural modes was measured in the frequency range 8 kHz to 68 kHz.

the corresponding integrals over these co-ordinates can be carried out in (3). Conservation of probability yields the value unity in each case. We are left with

$$\langle \epsilon_{ij}(x, t)\rangle = \beta\, C v_0\, \lambda^2\, \delta_{ij}\, (\mathrm{Tr}\, \sigma^0) \int_0^L dx'\, (1-2\, (x'/L))$$

$$\cdot \left(x' \middle| 1 - P_d^{\mathrm{eq}}(t) \middle| x\right), \tag{7}$$

where the matrix element $\left(x' \middle| P_d^{\mathrm{eq}}(t) \middle| x\right)$ is the solution of the equation

$$\partial f(x, t)/\partial t = D\, \partial^2 f(x, t)/\partial x^2, \tag{8}$$

subject to the initial condition

$$f(x, 0) = \delta(x-x') \tag{9}$$

and the boundary conditions

$$\partial f(x, t)/\partial x = 0 \quad \text{at } x = 0,\ x = L. \tag{10}$$

The last equation expresses the vanishing of the diffusion current on the faces of the specimen, i.e. the condition that no defects diffuse *out* of the material. The solution appropriate to the above initial and boundary conditions is

$$\left(x' \middle| P_d^{\mathrm{eq}}(t) \middle| x\right) = (1/L) + (2/L) \sum_{\mu=1}^{\infty} \cos(\mu\pi x'/L) \cos(\mu\pi x/L) \times$$

$$\exp(-\pi^2 \mu^2 Dt/L^2). \tag{11}$$

We note that this probability density is properly normalized.* Substituting this in (7) and evaluating the integrals, we obtain finally

$$\langle \epsilon_{ij}(x, t)\rangle = \beta\, C v_0\, \lambda^2\, \delta_{ij}\, (\mathrm{Tr}\, \sigma^0) \sum_{\mu=1,3\ldots}^{\infty} (8/\pi^2 \mu^2) \cos(\mu\pi x/L) \times$$

$$[1 - \exp(-\pi^2 \mu^2 Dt/L^2)], \tag{12}$$

where we have used also the Fourier cosine series expansion of the function $\sigma(x)$ defined in (4). Equation (12) is essentially equivalent to the result already found by Alefeld *et al* (1970), and serves to confirm the validity of our LRT approach and subsequent development of the theoretical formalism. The final, saturation value of the strain is

$$\langle \epsilon_{ij}(x, \infty)\rangle = \beta\, C v_0\, \lambda^2\, \delta_{ij}\, \mathrm{Tr}\, \sigma(x), \tag{13}$$

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*As $t \to \infty$, the probability of finding the diffusing particle in the range $(x, x+dx)$ becomes equal to (dx/L), independent of both the origin x' and of x itself, as we should expect on physical grounds.

corresponding to a relaxation strength proportional to λ^2 and inversely proportional to the temperature, as expected. The anelastic relaxation to this value proceeds via a whole set of relaxation times (Zener 1948; Alefeld *et al* 1970)

$$\tau_\mu = \tau/\mu^2, \ \mu = 1, 3, 5, \ldots, \tag{14}$$

where the fundamental relaxation time is

$$\tau = L^2/D\,\pi^2. \tag{15}$$

This is a consequence of the finite geometry* of the material, and reflects the fact that the anelasticity arises because of the *long-range* diffusion of the defects as opposed to local re-orientations. If we take $L^2 \sim 10^{-5}$ cm^2 and use the value (Wipf and Alefeld 1974) $D \sim 10^{-6}$ cm^2 sec^{-1} for H in Nb at room temperature, τ becomes ~ 1 sec, i.e., quite accessible experimentally. While the higher harmonics τ_μ represent even more rapid relaxation, the corresponding relaxation strengths are reduced by the factor $(1/\mu^2)$ in (12), and their contributions rapidly becomes negligible in a static experiment. However, there are two (related) situations in which it is not possible to approximate the process by one with a single relaxation time τ. For short times, i.e., $t \ll \tau$, the series in (12) converges very slowly, and we must look for a better representation for the strain. Correspondingly, in a dynamic experiment the frequency spectrum (of the loss tangent, for instance) will show a significant departure from the Lorentzian shape characteristic of a single relaxation time τ, in the region $\omega \gtrsim \tau^{-1}$. In fact, we can predict the high-frequency behaviour of the loss tangent quite easily from (12) itself. It is well known (see, e.g., Nowick and Berry 1972; also BDV) that a creep function of the form $(1 - \exp(-t/\tau))$ corresponds to a loss tangent of the form $\omega\,\tau\,(1+\omega^2\,\tau^2)^{-1}$ which peaks at $\omega\,\tau = 1$ and falls off as ω^{-1} for $\omega\,\tau \gg 1$. Corresponding to the multiple relaxation form of (12), the loss tangent is given by

$$\tan\phi\,(\omega) \propto \sum_{\mu=1,3,\ldots}^{\infty} (1/\mu^2)\,\omega\tau_\mu\,(1+\omega^2\,\tau_\mu^{\,2})^{-1}, \tag{16}$$

where $\tau_\mu = \tau/\mu^2$. Clearly, it is erroneous to write down the asymptotic ($\omega\,\tau \gg 1$) behaviour of this sum as a sum of the asymptotic forms of each term, as the resulting series no longer converges. However, we may approximate the sum by an integral over μ, and scale out the frequency dependence by a change of variables to $\mu' = \mu\omega^{-1/2}$ to obtain a leading high-frequency contribution that is proportional to $\omega^{-1/2}$ rather than ω^{-1}. Experimental values corroborate this prediction—see the analysis of Doremus (1971). We shall establish this result more firmly in the next section, where the response to a time-dependent stress is worked out.

2.3. *Short-time ($t \ll \tau$) behaviour and dynamic response*

Both the aspects mentioned above are studied by the same method of analysis. From a mathematical point of view, we need a different representation for the conditional

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*The surfaces of the slab act as reflecting barriers for the diffusing atoms.

probability $\left(x'\middle|P_d^{\mathrm{eq}}(t)\middle|x\right)$, i.e., for the solution of the differential equation (8), that is more suitable for the investigation of the small t region than the slowly converging series of (11). The use of Laplace transforms yields the required results: the details are outlined in Appendix A. The quantity of interest is the integral on the right in (7). Let us denote the Laplace transform variable (conjugate to the time t) by s, and introduce the dimensionless variable

$$\zeta = (L/2)\ (s/D)^{1/2} = (\pi/2)\ (s\tau)^{1/2}. \tag{17}$$

We then find that

$$\int_0^L dx' \left(1-2\frac{x'}{L}\right)\left(x'\middle|1-P_d^{\mathrm{eq}}(t)\middle|x\right) = \mathscr{L}^{-1}\left\{\frac{\sinh\ \zeta\ (1-2\ x/L)}{s\zeta\ \cosh\ \zeta}\right\}, \tag{18}$$

where $\mathscr{L}^{-1}$ stands for the inverse Laplace transform. Further manipulations lead to an expression for $\langle\epsilon_{ij}(x, t)\rangle$ that is quoted in Appendix A, (A.8). On the faces $x=0$ and $x=L$ this result takes on relatively simple forms. We find, for instance,

$$\langle\epsilon_{ij}(0, t)\rangle = 4\beta C v_0 \lambda^2 \delta_{ij} (\mathrm{Tr}\sigma^0)\ \Big[(t/\tau\pi^3)^{1/2} + \sum\nolimits_{\mu=1,\,2..}^{\infty} (-1)^\mu \times$$
$$\left\{(4t/\tau\pi^3)^{1/2} \exp\left(-\mu^2\pi^2\tau/4t\right) - \mu\ \mathrm{erfc}\left(\mu^2\pi^2\tau/4t\right)^{1/2}\right\}\Big]. \tag{19}$$

The *leading* term, for $t \ll \tau$, is the first one on the right in the square brackets, proportional to $t^{1/2}$. This behaviour is of course traceable to the assumption that the conditional probability $(x'\,|\,P_d^{\mathrm{eq}}(t)\,|\,x)$ obeys the diffusion equation, i.e., that Fick's law is valid. For free diffusion in a semi-infinite medium under such an assumption the rms displacement is well known to be $\sim t^{1/2}$. As t increases to become comparable to τ, the effect of the boundaries of the medium begins to be felt, and the other terms in (19) begin to contribute significantly.*

Now let us turn to the determination of the *exact* expression for the strain response to an applied stress of frequency ω, as in (I. 4). We may take the amplitude $\sigma_{kl}(\mathbf{R})$ to have the same spatial variation across the sample as in (4). Retaining only the dilatory part of the dipole tensor (for reasons already explained), (I.16) reduces in the present instance to

$$F_{ij}(\mathbf{R}, \omega) = \beta C v_0\ \lambda^2 \delta_{ij}\ \Big[\mathrm{Tr}\sigma(R) + i\omega \int_0^\infty dt' \exp\left(i\omega t'\right) \times$$
$$\int d\mathbf{R}'\, \mathrm{Tr}\sigma\ (\mathbf{R}')\ (\mathbf{R}'\,|\,P_d^{eq}(t')\,|\,\mathbf{R})\Big]. \tag{20}$$

Using the fact that the Fourier-Laplace transform of unity is i/ω (the analytic continuation of the corresponding Laplace transform to $s = -\ i\omega$), we obtain

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[*] The leading $t^{1/2}$ behaviour of the creep function at once leads to the prediction that the $\omega \to \infty$ behaviour of the complex compliance $J(\omega)$ is $\sim \omega^{-1/2}$: we have merely to use the relation between the response and relaxation functions, which reads $J(\omega) = -i\omega\ \bar{\phi}(\omega)$ in the present problem (see equation (2) of BDV). Here $\bar{\phi}(\omega)$ is the Fourier-Laplace transform of $\bar{\phi}(t)$. In Appendix B, we show how (27) below follows directly from (12), on exploiting this relationship.

$$F_{ij}(x,\omega) = -\,\beta C v_0 \lambda^2 \delta_{ij}(\mathrm{Tr}\,\sigma^0) i\omega \int_0^\infty dt' \exp(i\omega t') \int_0^L dx'(1-2x'/L) \times$$
$$(x' \,|\, 1-P_d^{\mathrm{eq}}(t') \,|\, x). \tag{21}$$

Again exploiting the relationship between Fourier-Laplace and Laplace transforms, we get with the help of (18),

$$F_{ij}(x,\omega) = \beta C v_0 \lambda^2 \delta_{ij}(\mathrm{Tr}\,\sigma^0) \sinh\,[\zeta\,(1-2x/L)]/\zeta \cosh \zeta, \tag{22}$$

where (since s is now identified with $-i\omega$) ζ stands for

$$\zeta = (\pi/2)\,(-i\omega\tau)^{1/2} = (\pi/2)\,(\omega\tau)^{1/2} \exp\,(-i\pi/4) \tag{23}$$

Therefore the anelastic strain caused by the long-range diffusion of defects under the application of a stress

$$\sigma(x,t) = \sigma^0\,(1-2x/L)\cos \omega t \tag{24}$$

is given by

$$\langle \epsilon_{ij}(x,t)\rangle = \beta C v_0 \lambda^2 \delta_{ij}(\mathrm{Tr}\,\sigma^0) \times$$
$$\mathrm{Re}\left\{\frac{\sinh \zeta(1-(2x/L))}{\zeta \cosh \zeta} \exp\,(-i\omega t)\right\}, \tag{25}$$

with ζ as in (23).

We may verify, first, that the above is consistent with the result derived earlier for a static stress field. The $\omega \to 0$ limit of (25) reads

$$\langle \epsilon_{ij}(x,t)\rangle \xrightarrow[\omega\to 0]{} \beta C v_0 \lambda^2 \delta_{ij}(\mathrm{Tr}\,\sigma^0)\,(1-2x/L), \tag{26}$$

which matches the saturation value ($t\to\infty$ limit) of the expression in (12), as required. Let us now compute the internal friction corresponding to (25). For simplicity (and in accordance with the experimental procedure) we may restrict ourselves to the face $x=0$ of the specimen. Consider the 11-component of the strain (i.e., the extension in the x-direction). On including the instantaneous or elastic response, the complex compliance is given by

$$J = M_U^{-1} + \beta C v_0 \lambda^2 \tanh \zeta/\zeta, \tag{27}$$

where M_U is the (unrelaxed) elastic modulus of the host material. The internal friction is defined as the argument of this complex quantity. Remembering that we are working correct to $O(1/T)$ we get

$$\tan \phi(\omega) = \beta C v_0 \lambda^2 M_U\, \mathrm{Im}\,(\tanh \zeta/\zeta)$$
$$= \beta C v_0 \lambda^2 M_U \frac{(\sinh 2\alpha - \sin 2\alpha)}{4\alpha(\sinh^2 \alpha + \cos^2 \alpha)}, \tag{28}$$

where $\alpha = (\pi^2 \omega\tau/8)^{1/2} = (\omega L^2/8D)^{1/2}.$ (29)

An essentially equivalent result for the internal friction has been derived earlier by Doremus (1971) by a somewhat different and more restricted technique;* the experimental data of Cantelli *et al* (1970) on H in V have been fitted to the above functional dependence on ω and satisfactory agreement obtained. A brief comparison may be made of (28) with the alternate expression for $\tan \phi(\omega)$ that is obtainable from the response to a static stress (eq. (12)) on going over to its Fourier-Laplace transform, as indicated in a footnote in the foregoing (See also Appendix B). We find

$$\tan \phi(\omega) = \beta C v_0 \, \lambda^2 M_U \sum\nolimits_{\mu=1,3,..}^{\infty} 8\omega\tau/\pi^2\mu^4(\mu^4+\omega^2\tau^2). \tag{30}$$

In the low frequency limit ($\omega\tau \ll 1$), the leading behaviour predicted by (28) is

$$\tan \phi(\omega) \approx \beta C v_0 \lambda^2 M_U L^2 \omega/12D. \tag{31}$$

This is matched very closely by the value obtained from (30) on retaining the first ($\mu=1$) term above, the factor (1/12) being replaced by ($8/\pi^4$), which is a relative error of only 1·4%. Approximating the process by one with a single relaxation time (Alefeld *et al* 1970) is therefore quite justified in this frequency region. However, as $\omega\tau$ increases, this approximation becomes increasingly poor. The asymptotic ($\omega\tau \gg 1$) value of $\tan \phi(\omega)$ is, as we have seen already, proportional to $\omega^{-1/2}$ in contrast to the ω^{-1} behaviour predicted by a single relaxation time approximation. The exact leading asymptotic behaviour is found from (28) to be

$$\tan \phi(\omega) \approx \beta \, C v_0 \, \lambda^2 \, M_U \, (2 \, D/\omega \, L^2)^{1/2} \; (\omega \, \tau \gg 1). \tag{32}$$

In figure 2, we plot $\tan \phi(\omega)/\beta C v_0 \lambda^2 M_U$ as a function of $\omega\tau$ both for the exact result of (28) and for the approximate one obtained by retaining only the $\mu=1$ term in (30), for the purposes of comparison. As the abscissa is on a logarithmic scale, we may regard this also as a plot of the function against the reciprocal of the temperature at a fixed value of ω, if the Arrhenius form for the temperature dependence of D is assumed to be valid. It is the curve predicted in (28) that seems to fit (Doremus 1971) experimental values (Cantelli *et al* 1970) better. However, it must be mentioned here that the temperature dependence of the diffusion coefficient D of H in Nb is itself a peculiar one (Völkl and Alefeld 1976). Both the prefactor D_0 and the activation energy U show a break in the range —50°C to 0°C, so that the actual T-dependence of $\tan \phi(\omega)$ is quite involved.

3. Ultra-high frequency response

3.1. *Statement of the problem*

A salient feature of the foregoing is the conclusion that the asymptotic ($\omega\tau \gg 1$) behaviour of the internal friction associated with diffusion relaxation is $\sim (\omega\tau)^{-1/2}$, in marked contrast to the $(\omega\tau)^{-1}$ fall-off corresponding to a Lorentzian spectrum (or a

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*The diffusion equation in the presence of a pressure applied across the faces of the slab with frequency ω and constant spatial gradient is solved approximately (after 'linearization') by an ansatz. Various minor errors in the result obtained there are rectified in (28). Our result is of course a by-product of a general theory, and it also explicitly relates $\tan \phi(\omega)$ to the microscopic parameter λ.

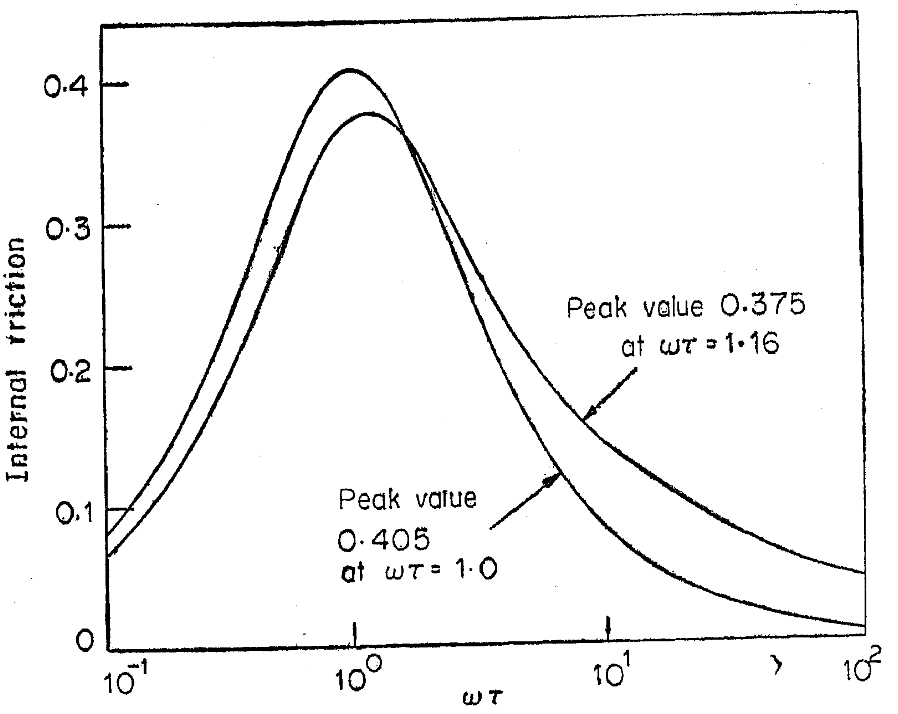

Figure 2. Frequency dependence of internal friction for diffusion relaxation shown in plot of tan $\phi(\omega)/\beta\, Cv_0 \lambda^2 M_U$ against $\omega\tau$, with $\tau = L^2/D\pi^2$. (a) Exact expression (equation (28)); (b) single relaxation time approximation. Since the abscissa is on a log scale, the plot is also a variation of the internal friction with T^{-1} at fixed ω (as usual). Experiment fits curve (a). At ultra-high values of ω (not shown), we predict a true ω^{-1} fall-off instead of the $\omega^{-1/2}$ tail of curve (a), because of departures from the simple diffusion equation model.

superposition of a finite number of these). This result, borne out by experiment, is really a consequence of the short-time behaviour of the solution of the diffusion equation (5), i.e., of a process obeying Fick's law. Indeed, a convincing check of this assertion is as follows (as already mentioned in the footnote referred to earlier). Let us begin with the leading (small t) behaviour in (19), written in the form

$$\langle \epsilon_{11}(0, t) \rangle / \mathrm{Tr}\,(\sigma^0) \approx 4\beta\, Cv_0\, \lambda^2 (t/\pi^3 \tau)^{1/2}. \tag{33}$$

Then the relaxation-response relationship $J(\omega) = -i\omega\,\bar{\psi}(\omega)$ leads at once to*

$$\begin{aligned} \tan\phi(\omega) &\approx 4\beta\, Cv_0\, \lambda^2 M_U \,\mathrm{Im}\,[\Gamma(3/2) \exp(i\pi/4)(\pi^3 \omega\tau)^{-1/2}] \\ &= \beta\, Cv_0\, \lambda^2 M_U (2/\pi^2 \omega\tau)^{1/2} = \beta\, Cv_0\, \lambda^2 M_U (2D/\omega L^2)^{1/2}, \end{aligned} \tag{34}$$

which is precisely (32), as required.

While this frequency dependence is undoubtedly the correct one for $\omega\tau \gtrsim 1$, possibly for several decades of this quantity, the question arises as to whether this remains true at even higher frequencies. It is well known that the 'naive' diffusion equation (5) itself breaks down at ' short times ' when a careful examination of the microscopic

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*We use the fact that if $\psi(t) = t^\nu$, $\bar{\psi}(\omega) = i\,\Gamma(1+\nu) \exp(i\pi\nu/2)/\omega^{\nu+1}$.

processes involved reveals the existence of new time scales related to atomic dynamics. The most classic example of this phenomenon is of course that of Brownian motion (Chandrasekhar 1943), and the development of appropriate 'improved' models of diffusion in dense gases, liquids and solids is a subject in itself. We may note that such 'corrections' may become significant even for time intervals somewhat longer than the ultimate atomic time scales, for certain effective time scales may emerge from the underlying atomic processes by a kind of coarse graining. Again, this is familiar even in the elementary theory of the Brownian motion of a free particle. The extremely rapid molecular collision processes lead to a longer time scale specified by the inverse of the friction coefficient (or viscosity).* The question in the present context, therefore, is: with reference to the Gorsky effect due to the long range diffusion of H in metals, will an improved model of the mechanics of the diffusion process alter the behaviour of the anelastic response significantly (at high frequencies)? If so, what is the *correct* asymptotic behaviour of, say, the internal friction tan $\phi(\omega)$?

We shall show that the answer to the first question is in the affirmative. Further, we predict on very general grounds that tan $\phi(\omega)$ should ultimately exhibit a *crossover* back to a ω^{-1} fall-off, and we evaluate also the coefficient of this term (correct to a numerical factor expected to be roughly of the order of unity). Of some significance is the fact that this coefficient is determined in terms of the fundamental parameters governing the actual jump diffusion of the interstitials.

3.2. *Jump diffusion of H interstitials in Nb*

The phenomenon (e.g., see Völkl and Alefeld 1975) is one for which an exact analysis is a very complex problem, beset with a number of difficulties. Let us list some of the points that must be taken into account even in the case of the diffusion of a dilute interstitial gas of H atoms in the host bcc lattice:

(i) The H atoms occupy six inequivalent types of sites (of tetrahedral symmetry) per unit cell, as shown in figure 1. The interstitial lattice is a *non-regular* graph in three dimensions. This makes the combinatorics of a random walk analysis rather complicated, because there is no simple closed form for the corresponding generating function (see, for instance, Kasteleyn 1967; Gissler and Rother 1970; Gissler and Stump 1973).

(ii) The jump diffusion of H atoms is activated both thermally as well as quantum mechanically, tunnelling being facilitated by the random lowering of neighbouring potential minima by thermal fluctuations. The elementary step diffusion of a proton is thus a rather complicated affair (Flynn and Stoneham 1970; Stoneham 1972; Kehr 1976), among other things leading to complicated isotope effects (Richter *et al* 1977). There are at least two characteristic times, namely, the mean residence time of an H atom at an interstitial site, and the mean flight time between sites. In addition, there are local mode complications arising from the motion of an H atom about an interstitial lattice site.

We do not intend to tackle these problems in full here. Our aim is to derive a simple theory based on physical arguments that enables us to deduce the correct asymptotic behaviour of tan $\phi(\omega)$. The method used borrows relevant information

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*Some points (regarding time scales) pertinent to the above remarks are discussed in Kubo (1966), §8; especially see equation (8.11)–(8.16) in that section.

from a first-principles theory of interstitial diffusion (Balakrishnan and Venkataraman 1975, 1978) that is based on a two-state random walk model. (The latter is inspired by the model of Singwi and Sjölander (1960) developed for the diffusion of water molecules). We emphasize that only the results required for our immediate purposes will be quoted, in the interests of brevity.

For simplcity, let us replace the interstitial lattice by a regular cartesian graph in which each point has four nearest neighbours, at a distance equal to $a/2\sqrt{2}$ (a is the lattice constant of the host bcc lattice). This is the magnitude of the tetrahedral-tetrahedral step. The inaccuracy introduced by this approximation will be contained, essentially, in a numerical factor in the final result. Since the interstitial lattice is rather 'well connected', and not sparse, the factor will be roughly of the order of unity. For the purpose at hand, this approximation is not seriously questionable, and it permits an analytic solution to be obtained. Even after this simplification, the problem is formidable: the complicated discrete random walk model must be cast in the form of a difference equation for the jump diffusion, the continuum limit must be taken, and the resulting partial differential equation must be solved for the *finite* geometry of the specimen, to obtain the 'correct' expression for $\left(\mathbf{R}'\middle|P_d^{\text{eq}}(t)\middle|\mathbf{R}\right)$. However, we present a stratagem that circumvents these difficulties. It is well known that a careful treatment of the short-time behaviour of any diffusion process leads to a drastic alteration of the time dependence of the mean square displacement. This quantity is asymptotically equal to $6Dt$ (which essentially serves as a definition of the diffusion coefficient), but at short times switches from the linear t dependence (dictated by Fick's law) to a quadratic dependence. The physical reason for the latter is the 'free particle' behaviour of the diffusing entity for very short time intervals. An analysis of Brownian motion (Chandrasekhar 1943) shows, in fact, that the Van Hove self-correlation function* has the form

$$G_s(\mathbf{R}, t) = [2\pi g(t)]^{-3/2} \exp\,[-\mathbf{R}^2/2g(t)], \tag{35}$$

where the relationship $g(t) = 2Dt$ of the naive diffusion equation model is replaced by the functional form

$$g(t) = (2D/\gamma)\,[\gamma t - 1 + \exp(-\gamma t)]. \quad (t > 0) \tag{36}$$

Here γ is the (phenomenological) friction coefficient (or viscosity) that is introduced in the Langevin equation. The mean square displacement works out to be $3g(t)$. Using (36), this is seen to approach the value $6Dt$ for $\gamma t \gg 1$, but then to switch over to the value $3D\gamma t^2$ for $\gamma t \ll 1$. These results are occasionally expressed succinctly by the statement that, in an accurate treatment of the (classical) Brownian motion problem, the time variable t occurring in the results obtained from the diffusion equation must be replaced by the 'Chandrasekhar prescription'

$$t \to t' = [\gamma t - 1 + \exp(-\gamma t)]/\gamma. \tag{37}$$

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*We have denoted $G_s(\mathbf{R}, t)$ by $\left(\mathbf{0}\middle|P_d^{\text{eq}}(t)\middle|\mathbf{R}\right)$.

It is this fact that we shall exploit in order to write down the asymptotic behaviour of tan $\phi(\omega)$, by identifying the correct modification of the t-dependence of the right hand side of (33).

3.3. *Asymptotic behaviour of the internal friction*

In Appendix C, we give a brief account of the relevant portions of the two-state random walk model of the jump diffusion of interstitials referred to earlier. It is shown there, in (C. 8) and (C. 10), that the correct short-time 'prescription' in the sense of (37) in the present problem is

$$Dt \to a^2 w_L t^2 \dot{p}\dot{q}/96\,(w_L+w_F) = \tfrac{1}{2}\, w_L \dot{p}\dot{q} D t^2. \tag{38}$$

Here a is the lattice constant of the host bcc lattice. The quantities $\dot{p}$ and $\dot{q}$ stand for certain transition probabilities (see Appendix C): each interstitial atom may be in one of two 'states' at any given instant of time—a state L in which it is localised about an interstitial lattice site, or a state F in which it is in flight between two such sites. *Given* that it is in state $L[F]$ at time 0, the probability that it continues to be in the *same* state at time t is $p(t)$ $[q(t)]$. Thus the $L \to F$ transition probability per unit time is given by $-\dot{p}(t)$ while for $F \to L$ it is given by $-\dot{q}(t)$. In (38), $\dot{p}$ and $\dot{q}$ stand for the derivatives evaluated at $t=0$. Further,

$$w_L = \int_{-\infty}^{0} dt\, p(|t|) = \int_{0}^{\infty} dt\, p(t), \tag{39}$$

and w_F is defined similarly with $q(t)$ replacing $p(t)$. The ratios $w_L/(w_L+w_F)$ and $w_F/(w_L+w_F)$ represent the *a priori* probabilities of the initial $(t=0)$ state being L and F respectively.

Remembering that $\tau = L^2/D\pi^2$, if we effect the substitution (38) in (33), we obtain

$$\frac{\langle \epsilon_{11}(0,t)\rangle}{(\mathrm{Tr}\,\sigma^0)} \approx \beta\, C v_0\, \lambda^2 \left\{\frac{a^2 w_L \dot{p}\dot{q}}{6\pi L^2 (w_L+w_F)}\right\}^{1/2} t, \tag{40}$$

or, if we retain the D or τ dependence explicitly,

$$\frac{\langle \epsilon_{11}(0,t)\rangle}{(\mathrm{Tr}\,\sigma^0)} \approx \beta\, C v_0\, \lambda^2 \,(8 w_L \dot{p}\dot{q}/\pi^3\tau)^{1/2}\, t. \tag{41}$$

The corresponding asymptotic behaviour of the internal friction is then given by

$$\tan\phi(\omega) \approx \beta C v_0\, \lambda^2 M_U\, (8 w_L \dot{p}\dot{q}/\pi^3\tau)^{1/2}\, \omega^{-1} \tag{42}$$

instead of the expression in (34). This is the required result.

3.4. *Discussion*

The complicated physics of the interstitial jump phenomenon is contained in the parameters $\dot{p}$, $\dot{q}$ and w_L. We do not go into the question of the temperature dependence

Appendix A

Laplace transform solution of the diffusion equation

The one-dimensional diffusion equation (8), with the initial condition (9), is solved easily with the help of Laplace transforms. Defining

$$\bar{f}(x,s) = \mathscr{L}\,[(f(x,t)] = \int_0^\infty dt\, f(x,t)\exp(-st), \tag{A.1}$$

we obtain, on using the initial condition,

$$\partial^2 \bar{f}(x,s)/\partial x^2 = (s/D)\,\bar{f}(x,s) = -(1/D)\,\delta(x-x'). \tag{A.2}$$

This is just the differential equation satisfied by the Green function of the operator $(s - D\partial^2/\partial x^2)$, so that the solution can be written down in terms of the solutions of the homogeneous equation. Incorporating the boundary conditions (10), the result is

$$\begin{aligned}\bar{f}(x,s) = (kD\sinh kL)^{-1}\,[&\cosh kx\cosh k(L-x')\,\theta(x-x')\\ &+\cosh k(L-x)\cosh kx'\,\theta(x'-x)],\end{aligned} \tag{A.3}$$

where $k^2 = s/D$. The inverse Laplace transform $f(x,t)$ may be written down in terms of series of error functions. However, we are actually interested in the integral

$$\int_0^L dx'\left(1-2\frac{x'}{L}\right)f(x,t) = 1-\frac{2}{L}\int_0^L dx'\,x'\,f(x,t). \tag{A.4}$$

Therefore we may carry out the integration over x' using $\bar{f}(x,s)$ in the integrand and *then* inverting the Laplace transform. The integration yields

$$\int_0^L dx'\,\bar{f}(x,s) = (x/s) + \sinh k\,(\tfrac{1}{2}L - x)/(ks\cosh\tfrac{1}{2}kL). \tag{A.5}$$

Since the inverse Laplace transform of $(1/s)$ is unity, it follows immediately that

$$\begin{aligned}&\int_0^L dx'\left(1-2\frac{x'}{L}\right)\left(x'\,\middle|\,\mathbf{1}-P_d^{\mathrm{eq}}(t)\,\middle|\,x\right)\\ &\quad=\frac{2}{L}\mathscr{L}^{-1}\left\{\frac{\sinh k\,(\frac{1}{2}L-x)}{ks\cosh\frac{1}{2}kL}\right\}.\end{aligned} \tag{A.6}$$

This is the result quoted in (18) of the text in terms of the variable $\zeta = (kL/2)$. As shown in (21), the response to an applied stress of frequency ω is essentially the Fourier-Laplace transform of the integral on the left in (A.6). It is therefore identically equal to the analytic continuation to $s = -i\omega$, i.e., to $k = (\omega/D)^{1/2}\exp(i\pi/4)$, of the expression in curly brackets on the right-hand side in this equation.

To obtain an expression for the response to a time independent stress that is particularly useful for $t \lesssim \tau$, we must first use the expansion

$$\operatorname{sech} \tfrac{1}{2}kL = 2 \exp\left(-\tfrac{1}{2}kL\right) \sum\nolimits_{\mu=0}^{\infty} (-1)^{\mu} \exp(-\mu kL) \tag{A.7}$$

in (A.6), and invert the Laplace transform term by term. Using standard results on Laplace transforms (Oberhettinger and Badii 1973), (7) is brought finally to the form

$$\begin{aligned} \langle \epsilon_{ij}(x, t) \rangle = 2\beta C v_0\, \lambda^2\, \delta_{ij}\, (\mathrm{Tr}\, \sigma^0) \sum\nolimits_{\mu=0}^{\infty} (-1)^{\mu}\, & [(4t/\pi^3\tau)^{1/2} \times \\ & \{\exp[-(\mu + x/L)^2\, \pi^2\tau/4t] - \exp[-(\mu + 1 - x/L)^2\, \pi^2\tau/4t]\} \\ & + (\mu + 1 - x/L)\, \mathrm{erfc}\, \{\tfrac{1}{2}\pi\, (\mu + 1 - x/L)(\tau/t)^{1/2}\} \\ & - (\mu + x/L)\, \mathrm{erfc}\, \{\tfrac{1}{2}\pi\, (\mu + x/L)\, (\tau/t)^{1/2}\}]. \end{aligned} \tag{A.8}$$

where $\tau = L^2/D\pi^2$. The special case $x = 0$ is easily simplified to yield (19).

Appendix B

Direct evaluation of $J(\omega)$ from the creep function

We show how the relation $J(\omega) = -i\,\omega\, \bar{\psi}(\omega)$ between the response and relaxation functions may be used to find $J(\omega)$ directly from $\psi(t)$. (Tensor indices have been suppressed). Specifically, we begin with (12) written as

$$\frac{\langle \epsilon_{11}(0, t) \rangle}{(\mathrm{Tr}\, \sigma^0)} = \psi(t) = \beta C v_0 \lambda^2 \sum\nolimits_{\mu=1,\,3 \ldots}^{\infty} \left(\frac{8}{\pi^2 \mu^2}\right) (1 - \exp(-\pi^2 \mu^2 Dt/L^2)), \tag{B.1}$$

with the aim of obtaining the anelastic compliance expressed in (27). We have

$$\begin{aligned} -\,i\omega\, \bar{\psi}(\omega) &= -\,i\omega \int_0^{\infty} dt \exp(i\,\omega t)\, \psi(t) \\ &= (8\beta\, C v_0\, \lambda^2/\pi^2) \sum\nolimits_{\mu=1,\,3,\ldots}^{\infty} (\mu^2 - i\omega\tau)^{-1}. \end{aligned} \tag{B.2}$$

The sum is evaluated by means of a Sommerfeld-Watson transform. Consider the integral

$$I = (2\pi i)^{-1} \int_C dz \exp(i\pi\, (z-1)/2)\, \sec\, (\pi z/2)\, (z^2 - i\omega\,\tau)^{-1} \tag{B.3}$$

where C is a hairpin contour encircling the poles of $\sec(\pi z/2)$ at $z = 1, 3, \ldots$ on the positive real axis in the clockwise sense. Since the integrand vanishes sufficiently rapidly as $|z| \to \infty$ along any ray in the upper or lower half plane, C may be distorted to a hairpin contour C' encircling the poles at $z = -1, -3, \ldots$ in the anticlockwise sense, *plus* small circles encircling (in the positive sense) the poles of the integrand at $z = \pm (i\omega\tau)^{1/2}$. Now

$$I = (2/\pi) \sum_{\mu=1,3\ldots}^{\infty} (\mu^2 - i\omega\tau)^{-1}, \tag{B.4}$$

while $\int_C = -\int_{C'}$. Some simple algebra then yields

$$J(\omega) = -i\omega\, \bar{\psi}(\omega) = (\beta C v_0 \lambda^2 \tanh \zeta)/\zeta, \tag{B.5}$$

where $\zeta = \frac{1}{2}\pi(-i\omega\tau)^{1/2}$, which is exactly equal to the anelastic contribution in (27).

Appendix C

Mean square displacement in interstitial jump diffusion

We give here a very brief outline of the relevant portions of the theory of jump diffusion on an (empty) lattice (Balakrishnan and Venkataraman 1975, 1978) that is based on a two-state random walk analysis. Consider, for simplicity, a cartesian lattice graph with points labelled by $\mathbf{l}=(l_1, l_2\ldots)$ where $l_i=0, \pm 1, \ldots$ A particle diffuses through this lattice by jumping from site to site along the bonds connecting them. At any instant of time, it may be in one of two states: either in mid-flight between two sites (state F), or engaged in localized motion about a site (state L). Let us define a *complete step* as a sequence of events that may be denoted by $L \to F \to L$. Then the possible zero-step processes are F, FL, FLF, L and LF; the one-step processes are $FLFL$, $FLFLF$, LFL and $LFLF$; and so on for $n > 1$. The question to be answered is: what is the (normalized) probability $W(n, t)$ of the particle executing n steps in a time interval t ? Once this is known, the Van Hove self-correlation function $G_s(\mathbf{R}, t)$ in the classical limit (which we have denoted by $(\mathbf{0}\,|\,P_d^{\mathrm{eq}}(t)\,|\,\mathbf{R})$) can be determined using combinatorics specific to the lattice concerned. For a random walk starting from the lattice point $\mathbf{0}$ (or from a bond attached to it, and going through $\mathbf{0}$ as the first stop) to the lattice point $\mathbf{l}$ (the position $\mathbf{R}$ being at this site or on a bond attached to it), we find

$$G_s(\mathbf{R}, t) = \sum_{n=0}^{\infty} W(n, t)\, P_n(\mathbf{l}). \tag{C.1}$$

Here $P_n(\mathbf{l})$ is the combinatorial factor that gives the probability of reaching $\mathbf{l}$ from $\mathbf{0}$ in exactly n steps. We must also include in $W(n, t)$ the *a priori* probability of the initial state of the particle being L or F. It is convenient to work with generating functions. Let us denote that of $P_n(\mathbf{l})$ by $[Q(z)]^n$; for unbiased single step jumps on a simple cubic lattice, for instance, $Q(z) = (1/6)(z_1 + z_1^{-1} + z_2 + z_2^{-1} + z_3 + z_3^{-1})$. Further, let $H(z; t)$ be the generating function of $W(n, t)$. Then the generating function of $G_s(\mathbf{R}, t)$ can be shown to be $H(Q(z); t)$, and the mean square displacement (in the absence of any bias or drift in the random walk) works out to

$$\text{RMS displacement} = a_s^2\, [\partial H(z; t) \,|\, \partial z]_{z=1} = a_s^2\, \nu(t), \tag{C.2}$$

where a_s is the step length and $\nu(t)$ is the mean number of steps taken in time t. It remains to work out an expression for $W(n, t)$ and hence for $H(z; t)$, from first principles. Let us assume that the switching processes from state L to state F and vice versa are stationary random processes; given that the particle is in state L at time t_0, let $p(t-t_0)$ be the probability that it continues to be in the same state at time t (regardless of its earlier history); similarly, given that it is in state F at t_0, let $q(t-t_0)$ be the probability that it continues in the same state at time t. Evidently, $p(0)=q(0)=1$, and $p(t)$, $q(t)$ are positive quantities for $t>0$. Before writing down the expressions for the chains contributing to $W(n, t)$, we must decide on the *a priori* probability factor for the particle to be in state L (or F), from physical grounds. The most appropriate choice is to weight the initial state by taking account of cumulative past history as contained in the integrals

$$w_L = \int_{-\infty}^{0} dt'\, p(|\,t'\,|) = \int_0^{\infty} dt'\, p(t'), \quad \text{and} \tag{C.3}$$

$$w_F = \int_{-\infty}^{0} dt'\, q(|\,t'\,|) = \int_0^{\infty} dt'\, q\,(t'). \tag{C.4}$$

The relative probabilities for initial states L and F respectively are then $w_L/(w_L+w_F)$ and $w_F/(w_L+w_F)$. Further, the transition probabilities per unit time for $L \rightarrow F$ and $F \rightarrow L$ are $-\dot{p}(t)$ and $-\dot{q}(t)$ respectively. The expression for $W(0, t)$ is then a sum of the probabilities for the five processes listed earlier, and reads

$$\begin{aligned}(w_L+w_F)\, W(0, t) = w_F\Big[q(t) - \int_0^t dt_1\, p(t-t_1)\, \dot{q}\,(t_1) \\ + \int_0^t dt_2 \int_0^{t_2} dt_1\, q(t-t_2)\, \dot{p}\,(t_2-t_1)\, \dot{q}\,(t_1)\Big] \\ + w_L\Big[\, p(t) - \int_0^t dt_1\, q\,(t-t_1)\, \dot{p}\,(t_1)\,\Big].\end{aligned} \tag{C.5}$$

The general probability $W(n, t)$ $(n \geqslant 1)$ is a sum of four multiple integrals, corresponding respectively to sequences *FLF...LF*, *FLF...L*, *LF...LF*, and *LF...L*. A scaling of the variables shows that, to evaluate $\nu(t)$ correct to $O\,(t^2)$, it is sufficient to consider $W(0, t)$ and $W(1, t)$. We find, after simplification, that

$$\nu\,(t) = \tfrac{1}{2}\, w_L\, \dot{p}\, q\, t^2/(w_L+w_F) + O\,(t^3) \tag{C.6}$$

where $\dot{p} \equiv [dp\,(t)/dt]_{t=0}$, and similarly for $\dot{q}$.

This result is sufficient for our purposes. The diffusion equation predicts, as we have already seen, that the rms displacement is equal to $6Dt$. On the other hand, at short times, we obtain from (C. 2) and (C. 6) the answer

$$\text{RMS displacement} = w_L\, \dot{p}\, \dot{q}\, a^2\, t^2/16\, (w_L+w_F), \tag{C.7}$$

on putting in the value $a_s = a/2\sqrt{2}$ for the tetrahedral-tetrahedral step in a host bcc lattice. Comparing this with $6Dt$, it is clear that the correct 'short-time prescription' is

$$Dt \rightarrow w_L\, \dot{p}\, \dot{q}\, a^2\, t^2/96\, (w_L+w_F). \tag{C.8}$$

It is this expression that is made use of in (33) to obtain (40) and the results that follow.

It is also possible to sum the series for the generating function $H(z; t)$, or at least for its Laplace transform $\bar{H}(z; s)$ in closed form. The behaviour of $\bar{H}(z; s)$ as $s \to 0$ yields the $t \to \infty$ behaviour of the theory, and we find (again in the absence of any bias in the random walk)

$$\nu(t) = t\,(w_L + w_F)^{-1} + O\,(1). \tag{C.9}$$

A comparison once again of (C.9) with the diffusion equation result shows that we may write (C.8) in the alternate form

$$Dt \to \tfrac{1}{2}\, w_L\, \dot{p}\, \dot{q}\, Dt^2. \tag{C.10}$$

This leads to the expression quoted in (41).

For completeness, we must mention here that a number of specific models of diffusion emerge as special cases of our general formalism. For instance, the jump diffusion model of Chudley and Elliott (1961) is an *instantaneous jump model*, i.e.,

$$-\dot{q}\,(t) \to \delta_+\,(t), \tag{C.11}$$

together with an exponential form $p\,(t) = \exp\,(-t/\tau_L)$, so that τ_L is the mean residence time at a site. This sort of model is incorrect at short times, suffering from the same deficiency as the solution of the diffusion equation. On the other hand, the retention of a finite mean flight time τ_F ensures the correct short-time behaviour of the theory. If we specialize to an exponential form for $q(t)$ as well, according to $q(t) = \exp\,(-t/\tau_F)$, then $w_L = \tau_L$ and $w^F = \tau_F$. We obtain a closed form for $\nu\,(t)$, namely,

$$\nu\,(t) = (t - \tau_F + \tau_F \exp\,(-t/\tau_F))\,/\,(\tau_L + \tau_F), \tag{C.12}$$

entirely from random walk theory. In the limit $\tau_F \to 0$ (instantaneous jumps) the Chudley-Elliott theory is recovered; while in the limit $\tau_L \to 0$, the correct ' Chandrasekhar prescription ' for the diffusion of a free particle (see (36) and (37) of the text) is obtained. The general closed form for $\bar{H}(z; s)$ makes it possible, of course, to analyse more detailed models as well.

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