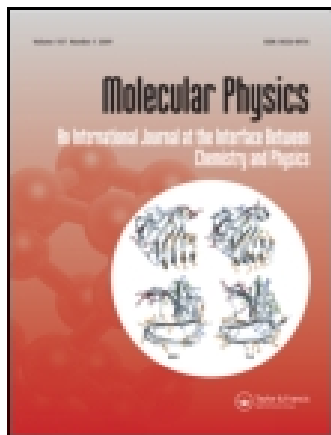


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Electrodynamics of amorphous media at low temperatures

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Amorphous solids exhibit intrinsic, local structural transitions, which give rise to the well-known quantum-mechanical two-level systems at low temperatures. We explain the microscopic origin of the electric dipole moment of these two-level systems: the dipole emerges as a result of polarization fluctuations between near degenerate local configurations, which have nearly frozen in at the glass transition. An estimate of the dipole's magnitude, based on the random first-order transition theory, is obtained and is found to be consistent with experiment. The interaction between the dipoles is estimated and is shown to contribute significantly to the Grüneisen parameter anomaly in low T glasses. In completely amorphous media, the dipole moments are expected to be modest in size despite their collective origin. In partially crystalline materials, however, very large dipoles may arise, possibly explaining the findings of Bauer and Kador [*J. Chem. Phys.*, **118**, 9069 (2003)].

1. Introduction

Glasses are frozen liquids and thus lack long-range order, yet the differences in material properties between amorphous materials and crystals are often rather subtle. Crystalline samples themselves are rarely flawless and thus contain a number of imperfections such as point defects, dislocations or grain boundaries of various sorts. These tend to further mask the difference. The size of defects in crystals ranges over many scales, while in glasses, the static heterogeneity in the atomic arrangement appears comparable to the molecular size itself. Simple molecular glasses thus seem perfect candidates for description as isotropic continuum, at long enough wavelengths. For instance at cryogenic temperatures, when the de Broglie wavelength of a thermal phonon at ~ 1 K exceeds the lattice spacing by three orders of magnitude or so, continuum theory would be thought to hold to high accuracy. Yet surprisingly, there clearly exist degrees of freedom numbering in great excess of the Debye density of states, leading to extra heat capacity and phonon scattering in all amorphous materials [1]. Here, we examine the electro-dynamics of these degrees of freedom.

Since Rayleigh scattering is too weak to account for the observed magnitude of sound attenuation in glasses, internal resonances must be invoked, in the form of *anharmonic* structural rearrangements, in order to explain the data. The well-known, empirical two-level system (TLS) theory presumes such resonances exist [2, 3]. Simply postulating a flat energy spectrum and a frequency independent coupling to the phonons accounts for all the gross features of the low T anomalies (for reviews, see [4–6]). Direct microscopic evidence of the two-level nature of such entities comes both from the phonon echo experiments [7] and, relatively recently, from single-molecule experiments at cryogenic temperatures (see e.g. [8]). At these temperatures, the TLS picture is internally consistent in so far as the structural transitions (ST) can be defined as *local*, and thus, tautologically, sufficiently *weakly* interacting. One may therefore speak of a multilevel system at the location of each transition whose behaviour reduces to a TLS behaviour at low enough T . We may call this a tunnelling centre (TC). In 1986, Freeman and Anderson [9] showed that the magnitude of the TLS density of states is apparently correlated with the phonon coupling. This results in a universality of the ratio of the phonon mean free path l_{mfp} to its wavelength λ : $l_{\text{mfp}}/\lambda \sim 150$, for all insulating glasses at $T \lesssim 1$ K. This universality seems hardly coincidental [10], however understanding the origin of the universality requires a microscopic picture of molecular motions

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in glasses. (The large size of the factor ~ 150 , too, was a puzzle [10]).

The random first-order transition (RFOT) theory of the glass transition [11–15] provides an appropriate microscopic picture of the motions in glass. Most commercial and laboratory glasses are made by quenching supercooled melts. In the deeply supercooled regime, most liquid motions are activated transitions between distinct aperiodic states of comparable energy, during which the current structural arrangement in a *local* region is replaced by another, quite different arrangement that nevertheless fits its environment. The size of the reconfigurable region, ξ , grows with decreasing temperature, and reaches about 5–6 molecular units across by T_g , i.e. the glass transition temperature corresponding to the 1 h time scale. This size is predicted to be universal, within logarithmic accuracy, for *all* substances. At any point in time, above T_g , the liquid can be thought of as a mosaic of such cooperative regions [14], most of nearly the same size, but otherwise with distributed barrier heights and transition energies. Upon freezing, a particular mosaic pattern sets in and undergoes relatively slow changes, called aging. The aging speed depends on the quench depth [16]. A sufficient fraction of the structural transitions have small enough energy change and barriers so that when they occur, they can account for the cryogenic anomalies, some of which were mentioned above: the density of states and the universality of phonon scattering [17], the Boson peak [18], but also the anomalous Grüneisen parameter, the so-called ‘fast’ TLS systems and more [19, 20]. According to the RFOT theory, the universality of the l_{mfp}/λ ratio directly follows from the universal cooperative region size $(\xi/a)^3 \sim 200$ at the glass transition temperature T_g , where a is the molecular length scale. During a structural transition, a relatively large, ~ 200 , compact set of small units moves in a stage-wise fashion. This corresponds to the motion of the domain wall, which separates the two alternative arrangements, through the compact region. At cryogenic temperatures, these motions occur by tunnelling. Despite their collective nature, such tunnelling events are possible because of the enormous multiplicity of alternative structural states and of low-barrier paths connecting pairs of states: an amorphous sample actually resides in a high energy density state, well above its lowest energy, perfect crystalline state. Consistent with the facility of tunnelling is the smallness of individual atomic displacements during each transition. Their amplitude is roughly equal to the Lindemann length d_L . This length is typically one tenth of the characteristic lattice spacing a and is nearly the same for all substances. The precise identity of the ‘molecular unit’, or ‘bead’ depends on the specific substance, but usually corresponds to a

few atoms. (See [15] for a detailed discussion). The experimental evidence of the validity of the RFOT microscopic picture is overwhelming (for a review, see e.g. [20]). On the other hand, direct experimental verification of the multiparticle nature of the tunnelling events at *cryogenic* temperatures is difficult. For example, most scattering spectroscopies are largely insensitive to the length scale of *dynamic* heterogeneities, while nonlinear experiments are hard to realize at these temperatures. Computer modelling [21] unambiguously confirms the collective character of the tunnelling transition.

In this article, we use the microscopic picture of the two-level systems provided by the RFOT theory to estimate the coupling of the transitions to external electric fields. Clearly, such a coupling must be present because individual molecular bonds, that possess electric dipoles, rotate during transitions. Since these couplings directly enter into spectral hole-burning experiments [22] and can also be directly probed in single molecule experiments [8], it is important to know how such collective excitations interact electro-dynamically with probes and external electric fields.

2. Interaction of a single tunnelling centre with external field

2.1. Many-body origin of the transition-induced dipole moment

To set the stage, let us briefly review the assumptions of the traditional molecular models of dielectric response of insulating media. One often assigns an electric dipole value to an individual molecule, or to a molecular bond connecting distinct atoms in a condensed phase. In a dilute liquid made up of polar molecules, the medium polarizes in a field since the dipoles prefer to orient along the field’s direction at the cost of losing their rotational freedom. Even without permanent electric dipoles, a dielectric response occurs due to polarizability: an external field mixes in higher energy molecular orbitals, which generally lack inversion symmetry. Classically, this quantum mechanical response can be imitated as two harmonically bound opposite charges that separate after a field is turned on. In a polar substance, this polarizability also changes the *length* or *orientation* of the permanent dipoles.

While in a fluid the dipoles can freely reorient, during a structural transition (ST) in glass, the dipole is restrained: each individual bead within a tunnelling centre, or ‘domain’, moves only about the Lindemann length d_L , as illustrated in figure 1. Suppose, for the sake of argument, one can break up the set of all the beads within the domain into distinct pairs. (There is no loss of generality here, as will be pointed out at the end of

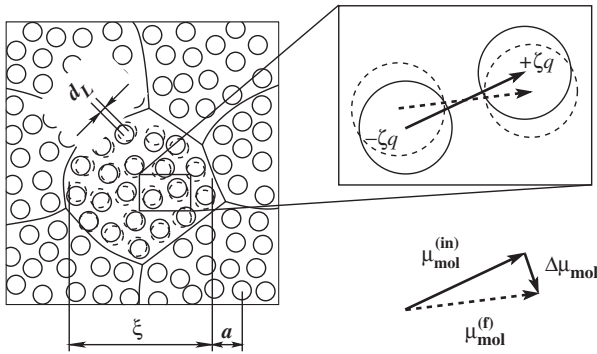


Figure 1. Shown on the left is a fragment of the mosaic of cooperatively reconfiguring regions in the supercooled liquid, with a denoting the lattice spacing (more precisely ‘bead’ spacing). ξ is the cooperative region size; d_L is the typical bead displacement during a transition. (The shown magnitude of ξ corresponds to a temperature near T_g on 1 h scale). The two sets of circles—solid and dashed ones—denote two alternative structural states. The expanded portion shows how rotation of a bond leads to generating an elemental dipole change during a transition, where the partial charges on the two beads are $\pm\zeta q$.

this subsection.) During a transition, each such pair—and hence the corresponding ‘bond’—rotates about $d_L/a \sim 0.1$ rad. The amorphous lattice generally exhibits no symmetry. There is, therefore, typically some excess charge, however small, on each atom. Assume the effective individual charges remain the same during such a transition. One can thus unambiguously assign a permanent, *point-like* electric dipole to each ‘bond’ introduced above. As schematically shown in figure 1, a total dipole moment, $\mu_T = \sum_i \Delta\mu_i$, may be generated during a structural transition, that would couple to an external electric field E with energy $-\mu_T E$.

In molecular glasses, the bond dipoles are fairly easy to assign. Generally, the assignment of point-like dipole moments to individual bonds is, strictly speaking, non-unique. It would be rather difficult in the case of a highly networked, covalently bonded substance, such as amorphous silica, but as we shall see, other arguments for such systems give similar results. These arguments use the measurable piezoelectric properties of corresponding crystals to unambiguously extract the coupling to fields. In weakly bonded molecular glasses held together by van der Waals forces, the point-like dipole view is already a good approximation.

With this in mind, an order of magnitude estimate of the dipole moment of a tunnelling centre can be made: the Coulomb charge on a bead does not exceed a fraction $\zeta < 1$ of an elementary charge q , which is close in magnitude to the electron charge e : $q \sim e$. An individual electric dipole *change* is therefore $\Delta\mu \sim \zeta\mu_{\text{mol}}(d_L/a)$, where (d_L/a) is the rotation angle, as already discussed, and $\mu_{\text{mol}} \equiv \zeta qa$ is the elemental dipole magnitude associated with each bond. The number of

pairs that reorient in a structural transition is $N_d = (\xi/a)^3/2$. The μ_T distribution is, of course, centred at the origin. Since the dipole forces are a small part of the energetics of the glass transition, the dipole motions are expected to be only weakly connected with each other. Therefore the individual dipoles $\Delta\mu_i$ make up a ‘random walk’ of N_d steps (in 3D). As a result, the generic value of dipole change for the transition is given by the width of the total displacements during such a walk:

$$\mu_T \simeq \zeta(qa)[(\xi/a)^3/2]^{1/2}(d_L/a). \quad (1)$$

If the elementary dipole rotations are correlated, one may introduce an additional factor—like the Kirkwood g factor of liquid theory [23]. g is typically of order 2. At first we might imagine a great deal of variability for the quantity $[(\xi/a)^3/2]^{1/2}(d_L/a)$ but in fact it is nearly universally (!) equal to unity for all substances. a is typically a couple of angstroms, implying qa corresponds to ~ 10 Debye. ($e \text{ \AA} \leftrightarrow 4.8$ Debye). ζ is expected to be well less than unity, with 0.1 or less being a reasonable generic estimate. We thus obtain that μ_T is of the order 1 Debye or less, consistent with experiment. Note the magnitude of μ_T is rather modest—only of the order of the size of a typical individual dipole moment—despite the large number of particles constituting a domain. The relative smallness of the two-level system dipole moment is due to the small deflection angle ~ 0.1 , and the apparent smallness of the partial charge ζq . There are deep reasons for both: the former stems from the particular magnitude of atomic displacements during a transition: it is equal to the typical thermal displacement at the mechanical stability edge, i.e. the Lindemann length [14]. The latter is probably related to the intrinsic difficulty of making ionically bonded aperiodic structures, which imposes an upper bound on the value of ζ ; this will be discussed in due time.

The sublinear scaling of the dipole moment with the domain volume ξ^3 , in equation (1), is worth noting: the tunnelling transition dipole moment is not a bulk response, and its relation to the material’s average bulk dielectric properties, as encoded, e.g. in the substance’s dielectric susceptibility $\epsilon(\omega)$ in the fluid phase, is not immediately obvious. While it is ultimately the deflections of the same elemental dipoles that both give rise to $\epsilon(\omega)$ and the dipole moment, the causes of the deflections differ. In contrast with the bulk polarizability, where the deflection magnitude is proportional to the field, the transition-induced deflections are intrinsic and correspond to distinct local structural states. (To illustrate this distinction further, we point out that a transition can be induced by things other than an AC (!) electromagnetic field—a thermal phonon for instance).

Above T_g , the distinct structural states, that evolve into TLS at cryogenic temperatures, are transient metastable structures that live typically as long as the α -relaxation time [14]. The transient structures are (transiently) frozen-in elastic fluctuations. Analogously, the intrinsic generated dipole moment may be thought of as due to frozen-in electric fields—at T_g . (A formal connection between generated electric field and mechanical stress is discussed in the following subsection). We can use this line of thought to relate the dipole moment to the bulk dielectric properties of the material near T_g . Suppose the frozen-in field is along the z direction. The corresponding dipole moment is related to this field via an appropriate (frequency dependent) dielectric constant $\epsilon_{\text{TLS}}(\omega)$, but also through the fluctuation-dissipation theorem. A self-consistent closure of this relationship gives for a spherical region of volume ξ^3 [24]:

$$-\frac{1}{k_B T_g} \int_0^\infty \exp(-i\omega t) \frac{d}{dt} \langle \mu_{T,z}(0) \mu_{T,z}(t) \rangle dt = \frac{[\epsilon_{\text{TLS}}(\omega) - 1][2\epsilon_{\text{ext}}(\omega) + 1]}{4\pi[2\epsilon_{\text{ext}}(\omega) + \epsilon_{\text{TLS}}(\omega)]} \xi^3, \quad (2)$$

where $\epsilon_{\text{ext}}(\omega)$ is the dielectric susceptibility outside the domain. The dielectric constant inside, $\epsilon_{\text{TLS}}(\omega)$, contains both the usual (high frequency) polarizability of the material and the polarization due to the dipolar displacements accompanying the transition. Even though the interior and exterior of the domain are chemically identical, it is necessary to regard the two ϵ 's as distinct, since we know a *transition* occurs within the volume ξ^3 . A similar relation can be written for the volume occupied by a single elemental dipole, with $\epsilon_{\text{ext}}(\omega) = \epsilon_{\text{TLS}}(\omega)$:

$$-\frac{1}{k_B T_g} \left(\frac{d_L}{a}\right)^2 \int_0^\infty \exp(-i\omega t) \frac{d}{dt} \langle \mu_{i,z}(0) \mu_{i,z}(t) \rangle dt = \frac{[\epsilon_{\text{TLS}}(\omega) - 1][2\epsilon_{\text{TLS}}(\omega) + 1]}{4\pi[3\epsilon_{\text{TLS}}(\omega)]} (2a^3), \quad (3)$$

where the factor $(d_L/a)^2$ on the left reflects that the elemental change in polarization, $\Delta\mu_i$, is related to the full elemental dipole μ_i by the rotation angle (d_L/a) , see figure 1. The volume $2a^3$ on the right corresponds to the volume occupied by a pair of beads, as before. One gets, as a result, a frequency dependent generalization of equation (1):

$$\langle \mu_T^{(2)}(\omega) \rangle = \langle \mu_i^{(2)}(\omega) \rangle [(\xi/a)^3/2] \left(\frac{d_L}{a}\right)^2 \times \frac{[2\epsilon_{\text{ext}}(\omega) + 1]3\epsilon_{\text{TLS}}(\omega)}{[2\epsilon_{\text{TLS}}(\omega) + 1][2\epsilon_{\text{ext}}(\omega) + \epsilon_{\text{TLS}}(\omega)]}, \quad (4)$$

where the two-point correlation functions are the t integrals above. Note $\langle \mu_T^{(2)}(0) \rangle = \langle \mu_T^2 \rangle$ and $\langle \mu_i^{(2)}(0) \rangle = \langle \mu_i^2 \rangle$. Finally, $\mu_i \simeq \zeta(qa) \equiv \mu_{\text{mol}}$, as before.

Note that two adjacent regions are statistically unlikely to undergo a structural transition at the same time. The physically preferable choice for the external dielectric susceptibility $\epsilon_{\text{ext}}(\omega)$ is therefore the high frequency, electronic component of the full dielectric response, which we call ϵ_∞ . With this, equation (4) becomes

$$\langle \mu_T^{(2)}(\omega) \rangle = \langle \mu_i^{(2)}(\omega) \rangle [(\xi/a)^3/2] \left(\frac{d_L}{a}\right)^2 \times \frac{[2\epsilon_\infty + 1]3\epsilon_{\text{TLS}}(\omega)}{[2\epsilon_{\text{TLS}}(\omega) + 1][2\epsilon_\infty + \epsilon_{\text{TLS}}(\omega)]}, \quad (5)$$

Furthermore, the two-level systems that are active at low temperatures correspond to the low barrier side of the barrier distribution. This implies one should use the $\epsilon_{\text{TLS}}(\omega \rightarrow \infty)$ value with regard to the cryogenic phenomena and, therefore, no extra frequency dependence appears in the coupling of the TLS to electric field. As a result, we find no significant reaction field correction to our earlier argument and obtain

$$\langle \mu_T^2 \rangle \simeq \mu_{\text{mol}}^2 [(\xi/a)^3/2] (d_L/a)^2, \quad (6)$$

cf. equation (1).

Finally, we point out that expression (1), for the transition dipole moment, is quite general in that it does not actually require invoking rigid dipoles, but only an overall electric neutrality of the domain. Moreover, equation (1) is asymptotically exact in the long wavelength limit and in the limit of small individual molecular displacements during a transition. Indeed, one may recall the standard expansion of the energy of a collection of charges in an external potential [25]: $U = \phi_0 \sum_i q_i + \mathbf{V}\phi_0 \sum_i q_i \mathbf{r}_i + \frac{1}{2} \sum_i q_i x_{i,\alpha} x_{i,\beta} \partial^2 \phi_0 / \partial x_\alpha \partial x_\beta + \dots$, where q_i are the individual charges and \mathbf{r}_i are their locations relative to some reference point labelled here with the naught. The transition dipole energy is given by the potential change during the transition, of course. The zeroth order term drops out because of neutrality. The first-order term scales with (kd_L) (\mathbf{k} being the wave-vector) and yields equation (1), with the same assumption on the randomness of the individual displacements. The second-order term is proportional to $(kd_L)^2$ and may be neglected for the relevant light wavelengths.

2.2. Piezoelectric view

To treat covalent network glasses, where the assignment of local dipoles or changes is difficult, we now turn

to a different way to relate the dielectric response, within a domain, to frozen mechanical stress. First consider a strictly periodic lattice that lacks parity symmetry. Generally, the lattice strain induces internal electric fields giving rise to piezoelectric behaviour. In such a piezoelectric, the energetics of the strain, in the lowest order, are described by the free energy density (see e.g. [26])

$$\tilde{F} = \frac{1}{2} \lambda_{ik,lm} u_{ik} u_{lm} - \frac{1}{8\pi} \epsilon_{ik} E_i E_k + \beta_{i,kl} E_i u_{kl}. \quad (7)$$

Here u_{ik} is the standard strain tensor [27], $\lambda_{ik,lm}$ and ϵ_{ik} are the stiffness tensor and the dielectric tensor, respectively, and $\beta_{i,kl}$ is a piezoelectric tensor. (Note, various sign conventions and free energies have been used in the literature.) The double index summation convention is implied throughout, with the exception of letters x , y and z , which will be obvious in the context. Finally, the elastic constant λ is related to the material's mass density ρ and the speed of sound c_s :

$$\lambda \sim \rho c_s^2. \quad (8)$$

In the absence of external field, $\mathbf{D} = -4\pi(\partial\tilde{F}/\partial\mathbf{E}) = 0$, the internal electric field is simply proportional to the strain itself:

$$E_i = 4\pi\epsilon_{ik}^{-1} \beta_{k,lm} u_{lm}. \quad (9)$$

(Note, the β tensor has the dimensions of electric field.) If expressed in terms of strain only, the free energy density reads, in the absence of external electric field:

$$\tilde{F} = \frac{1}{2} \lambda'_{ij,kl} u_{ij} u_{kl}, \quad (10)$$

$$\lambda'_{ij,kl} \equiv \lambda_{ij,kl} + 4\pi\epsilon_{mn}^{-1} \beta_{m,ij} \beta_{n,kl}. \quad (11)$$

The total, apparent stiffness, λ' , can be decomposed thereby into a purely 'covalent' and a 'Coulomb', i.e. electrostatic, component. The latter contribution is ordinarily quite small, owing to the smallness of the charges induced by lattice distortions. Consider α -quartz, for example. Here, only $\beta_{x,xx} = 5.2 \times 10^4$ esu and $\beta_{x,yz} = \beta_{x,zy} = (1/2)1.2 \times 10^4$ esu are non-zero [28]. As a result, the 'Coulomb' contribution to the (xx, xx) component of the apparent stiffness tensor is only about one percent of the covalent counterpart: $\lambda_{xx,xx} = 8.8 \times 10^{11}$ dyne cm^{-2} and $(4\pi/\epsilon_1^T) \beta_{x,xx}^2 = 7.4 \times 10^9$ dyne cm^{-2} . (Here, we used $\epsilon_1^T = 4.58$ [29]). The relative size of the λ versus β magnitudes can be

understood as follows: λ reflects the energy (density) of the elastic restoring force. It is essentially the second derivative of an individual atomic potential, with respect to the (dimensionless) strain u . Interatomic bonding, be it Coulombic or covalent in character, is ultimately of electrostatic origin. One may therefore associate λ with the quantity $(1/a^3)[\partial^2/\partial(r/a)^2](q^2/r)|_{r=a} = (q/a^2)^2$, where q is the effective charge giving rise to the bond, and the $1/a^3$ factor in front provides for energy density. (The total *first* derivative of the (full quantum) potential energy is zero, of course). By virtue of being an electric field, β roughly corresponds to the quantity q'/a^2 , where q' would be the partial charge introduced in the previous subsection. The ratio q'/q corresponds, within the present framework, to the earlier introduced quantity ζ . It follows that in α -quartz, the partial atomic charge is indeed about one tenth the elementary charge, since the quantity

$$\zeta^2 = (q'/q)^2 \simeq \beta^2/\lambda \quad (12)$$

is approximately equal to 1/100 in silica, as we just saw.

Now suppose for a moment that a relation similar to equation (9) exists between the bead displacements within a domain and the internal electric field changes generated during a transition. (We stress, in an amorphous sample such generated field changes are zero, upon spatial average, but here we refer to *local* fields at a particular, generally non-centrosymmetric site). Since $d\tilde{F} = -\mathbf{D}d\mathbf{E}/4\pi + \dots$, the free energy change in the presence of a (small) external field \mathbf{D}_{ext} during the transition is given by $\int_V dV \Delta\tilde{F} = -\mathbf{D}_{\text{ext}} \int_V dV \Delta\mathbf{E}/4\pi$, in the lowest order in \mathbf{D}_{ext} . (Here we have volume-integrated over the reconfiguring domain that corresponds with the two-level dynamics; \mathbf{D}_{ext} obviously varies sufficiently slowly within the domain for realistic frequencies of light, and can be taken out of the integral). The relation of the field \mathbf{D}_{ext} to the external field proper depends, of course, on the experiment's geometry. We will use an electric field $\mathbf{E}_{\text{ext}}(\mathbf{r}) = \epsilon^{-1}\mathbf{D}_{\text{ext}}(\mathbf{r})$, where ϵ is the average *bulk* dielectric susceptibility (which, of course, is uniform and isotropic in an amorphous material). The coupling to this field \mathbf{E}_{ext} is consequently given by

$$\mu_T = \frac{\epsilon}{4\pi} \int_V dV \Delta\mathbf{E}(\mathbf{r}), \quad (13)$$

i.e. the generated internal field difference during the transition, integrated over the domain. Equation (13), among other things, demonstrates that one may indeed unambiguously assign a collection of point-like dipoles

to the bead set within a TC, namely by virtue of the relation $\mathbf{E}(\mathbf{r}) = 4\pi c_1 \boldsymbol{\mu}(\mathbf{r})n(\mathbf{r})$, where $n(\mathbf{r})$ is the (coordinate-dependent) dipole concentration and the constant $c_1 \sim 10^0$ should be chosen depending on a specific way to incorporate the already mentioned cavity effects. In what follows, we will outline the microscopic picture of interaction of a transition with elastic strain, which will naturally lead us to the formula above and the ability to estimate the electric moment via a material's piezoelectric properties.

Since individual displacements \mathbf{d}_i during tunnelling transitions are only one-tenth of the lattice spacing, one can indeed describe the corresponding additional elastic energy variations, due to the presence of a phonon, by a quadratic form of the type from equation (7) or (10). Further, here one computes *relative* displacements, not the absolute atomic coordinates which are generally difficult to calculate. Define ϕ_{ik} as the strain tensor due to a (long-wave) lattice distortion of a stable lattice. In addition, define d_{ik} as the 'strain' tensor corresponding to the set of the tunnelling displacements $\{\mathbf{d}_i\}$. The full elastic energy within the domain, given a particular domain boundary configuration (call it Ω_b) can be written as

$$\tilde{F} = \frac{1}{2} \lambda'_{ij,kl} [(\phi_{ij} + d_{ij})(\phi_{kl} + d_{kl}) - d_{ij}d_{kl}] + \mathcal{H}(\{d_{ij}\}, \Omega_b), \quad (14)$$

where the energy functional $\mathcal{H}(\{d_{ij}\}, \Omega_b)$ includes all the nonlinear, many-body interactions giving rise to the existence of the many metastable structural minima within the domain. The construction of a library of the states corresponding to these minima was described in [16]. The full multiplicity of the local states reveals itself directly in calorimetric measurements above the glass transition. Here, we are only concerned with the two lowest energy states of a region of the otherwise undisturbed lattice. The two correspond to the two lowest minima of $\mathcal{H}(\{d_{ij}\}, \Omega_b)$. The size of the domain is, as we have seen, chosen so that one is guaranteed to have at least one alternative structural state of nearly the same energy, and was found to be only slightly larger than the cooperative region size at T_g [17]. Note, by construction, the boundary state Ω_b is independent of the phonon field ϕ_{ik} . The effect of an external *mechanical* stress on the internal displacements within a local, compact region is passed on through the boundary, and so the interaction of the region with the stress can be expressed through a displacement integral over the region surface [17, 20]. The cross $\lambda_{ij,kl}\phi_{ij}d_{kl}$ term in equation (10) gives the amount by which the energy of a tunnelling transition is modified by the presence of a phonon. This therefore gives the TLS–phonon coupling.

The latter coupling was estimated in this way in [17, 20]. A direct computation of the ϕ_{ij} -field-induced change of the transition energy gives: $\Delta E(\phi_{ij}) = \lambda'_{ij,kl}\phi_{ij} \int_V dV d_{kl}$, where we have integrated over the domain volume and taken advantage of the elastic strain being ϕ_{ij} nearly constant throughout the domain (λ' in the latter equation is the domain-averaged value of the atomic force-constant). The coefficient at the ϕ_{ij} gives a (tensorial) coupling of a transition to strain according to

$$\mathcal{H}_{\text{TLS,ph}} = g_{ij}\phi_{ij}\sigma_z, \quad (15)$$

where $\sigma_z = \pm 1$ is the usual Pauli matrix and

$$g_{ij} = \frac{1}{2} \lambda'_{ij,kl} \int_V dV d_{kl}. \quad (16)$$

This expression is consistent with the early microscopic estimates of the TLS–phonon coupling by Heuer and Silbey [30]. Now, the volume integral above indeed reduces to a surface integral of the tunnelling displacements. Consider for example, the term $\int_V dV d_{xy} = \int_S (d_x dx + d_y dy) dz$ etc. The coupling to the *longitudinal* phonons has the most vivid form, since d_{ii} is the divergence of a vector field, i.e. \mathbf{d} . One gets $g_{ii} \simeq \lambda \int_S \mathbf{d} \cdot \mathbf{dS}$. The atomic displacements at T_g are typically near the Lindemann length: $d \simeq d_L$, but can also be expressed in terms of the elastic constants, since the amount of elastic energy contained in a unit cell is determined by the temperature itself: $a^3 \lambda (d/a)^2 \sim T_g$. (This is by virtue of the fluctuation-dissipation theorem). Estimating the surface integral [17, 20] introduces additional numerical factors and gives, within a factor of two or so:

$$g \simeq (T_g \rho c_s^2 a^3)^{1/2}, \quad (17)$$

where we have used equation (8). The result above is easy to rationalize on general grounds: any atomic motions in a dense liquid (at T_g and otherwise) are either a vibration or an anharmonic motion that is part of a structural transition. The two excitations must coexist and thus be marginally stable against each other, in order for both to be present. Such a marginal stability criterion gives $\langle \sigma_z g_{ij} \phi_{ij} \rangle \simeq \langle \lambda_{ij,kl} \phi_{ij} \phi_{kl} \rangle$, as follows from optimizing equation (15) together with the elastic energy $\frac{1}{2} \lambda_{ij,kl} \phi_{ij} \phi_{kl}$ with respect to ϕ_{ij} , multiplying by ϕ_{ij} and thermally averaging (at $T = T_g$). Owing to $\langle \sigma_z \phi_{ij} \rangle \simeq \langle |\phi_{ij}| \rangle$, equation (17) follows.

In the same way that the elastic fluctuations interact with the atomic displacements, polarization waves and

external electric sources will interact with the internal electric fields generated in the domain during a transition. As we have seen, the mechanical response characteristics of a transition arise in response to stress fluctuations at T_g . Analogously we can say, the electric moments of the two-level system arise in response to the electric field fluctuations at T_g . In full analogy with the fluctuation-dissipation theorem context, the TLS dipole moment will interact with an external field source just as it did with the internal electric fields at the moment of freezing. We may thus compute the dipole moment by substituting the generated electric field from equation (9) into equation (13), bearing in mind that the local lattice and the corresponding tensors are no longer subject to any particular symmetry. Still, since the lattice locally resembles a crystalline lattice, one may choose coordinates, again locally, in such a way that the β tensor is maximally close to a crystalline one. (Clearly, the m, n sum in equation (11) is independent of the coordinate choice). Therefore, the latter sum will give a comparable result to that for a crystal. Summing over the displacement tensor d_{ij} (contracted with the β tensor) is quite analogous to the argument leading to equation (1). As a result one obtains the following qualitative estimate:

$$\mu_T \simeq (\bar{\beta}a^3)[(\xi/a)^3/2]^{1/2}(d_L/a), \quad (18)$$

where $\bar{\beta}$ is the local value of the piezoelectric coupling. (We remind the reader that glasses are on average isotropic and thus cannot have bulk piezoelectric properties. It is only in the frozen state that parity is locally broken). The simple relation

$$\xi qa \simeq \bar{\beta}a^3 \quad (19)$$

establishes the connection between the ‘molecular dipole’ view of the previous subsection and the ‘piezoelectric’ analysis in this subsection, cf. equation (12). Using the quartz parameters above, one obtains that μ_T is, again, of the order Debye. Note that formula (18) uses quantities that can be measured independently for substances which have a crystalline counterpart. The bead size a can be determined from the fusion entropy [15]. The piezoelectric constants are measurable too. The two views—one based on molecular moments, the other on local piezoelectricity—are somewhat distinct but are highly overlapping. Since the local hybridization pattern on individual atoms is intrinsically asymmetric in amorphous lattices, partial atomic charges, however small, are always expected to be present in glasses, giving rise to both local permanent

dipoles and local piezoelectricity. Mixing in a dipolar species would enhance both effects. According to [31], the two-level systems’s dipole magnitude is very correlated—nearly proportional—to the OH^- ion concentration, in amorphous silica with OH^- impurities. Yet extrapolation to small ion concentrations shows TLS in silica exhibit an *intrinsic* dipole moment, as was later confirmed by an electric dipole echo study [32].

2.3. Electrodynamics and electroacoustics: connection with experiment

In order to discuss experiments of two-level systems in glasses, involving external fields, let us first recapitulate a few aspects of the traditional phenomenological description, along with the microscopic explanation. The Hamiltonian of an isolated two-level system, as usually written in the low T glass context, is

$$\mathcal{H}_{\text{TLS}} = \frac{1}{2}\epsilon\sigma_z + \frac{1}{2}\Delta\sigma_x + g_{ij}\phi_{ij}\sigma_z, \quad (20)$$

where ϵ is the transition energy and Δ is the tunnelling matrix element. (The phonon part of the full Hamiltonian is given in equation (10)). According to [17, 18], the TLS that are thermally active at cryogenic temperatures have their splitting ϵ distributed according to a simple Boltzmann-like law $n(\epsilon) = (1/T_g) \exp(-\epsilon/T_g)$. This roughly defines the density of states of the tunnelling transitions. The density of states, as seen by calorimetry, is time dependent, because the tunnelling matrix elements Δ are widely distributed. According to the semi-classical analysis in [17, 18], the distribution is $P(\Delta) \propto 1/\Delta^{1+c}$, where $c \ll 1$ is a small constant ($c \propto \hbar\omega_D/k_B T_g$). This distribution is close to, but not precisely the same as the inverse distribution $\propto 1/\Delta$ postulated by the phenomenological TLS model. Including quantum effects reveals that the low splitting two-level systems, i.e. those with $\epsilon \ll \Delta$, are special in the following sense. In such regions, the excess strain energy of the glass is concentrated in the domain wall itself, while the barrier separating the two alternative structural states is not high enough to keep the domain in any of the classical structural states as defined in terms of the classical atomic coordinates. Such TLS, with depinned domain walls, give rise to an extra piece in the combined $P(\epsilon, \Delta)$ distribution [20]. They correspond to the so-called ‘fast’ two-level systems, introduced early on phenomenologically [33] in order to rationalize certain quantitative shortcomings of the original TLS model. The quantum depinning of the domain wall has been also called ‘quantum mixing’ [20]. Finally, we note the Hamiltonian in equation (20) leads to rich relaxational behaviour, due to both interaction

with phonons and the phonon-mediated interaction with other TLSs. This has been discussed in detail previously [3, 5, 34].

The effects of the interaction of the dipole moment with a *static* electric field are actually quite difficult to observe under routine laboratory conditions (see e.g. [35]). The upper limit for the field is given by the dielectric breakdown value and is generically 10^6 V cm^{-1} . For the typical dipole moment of 0.5 Debye, this implies an interaction energy of only $10^{-3} eV \sim 10 \text{ K}$. The constant field strength normally employed is actually an order of magnitude weaker, or less. In a field \mathbf{E}_{ext} , the transition energy is modified according to $\epsilon \rightarrow (\epsilon - \mu_{\text{T}}\mathbf{E})$. Typically, $|\mu_{\text{T}}\mathbf{E}| < 1 \text{ K}$. This is clearly inferior to the characteristic energy scale of the TLS spectrum, namely the glass transition temperature T_{g} [17]. The effect of a constant field thus turns out to be very generic because of the intrinsic flatness of the energy distribution: the angular part of $\mu_{\text{T}}\mathbf{E}_{\text{ext}}$ is, obviously, uniformly distributed resulting, again, in a flat distribution of the field-modified transition energy. In order to discern such a small energy variation, a *resonance* technique must be employed. Just such an experiment was performed by Maier *et al.* [22], who took advantage of the possibility to burn very narrow holes—only a few MHz—in the chromophore’s inhomogeneous spectrum. These authors turn on the field immediately after burning the hole and observe the (time-dependent) hole broadening, whose overall magnitude depends quadratically on the field strength. Maier *et al.* report the value of $\mu_{\text{T}} = 0.4 \text{ D}$ for a PMMA matrix.

It follows from our theory that light and sound couple to the two-level system transitions in a very similar way, save the dipole character of the TC–photon interaction distinct from the tensorial coupling of the transitions to the phonons. Indeed, the temperature dependence of the speed of light in vitreous silica, as obtained early on by von Schickfus *et al.* [36], nearly coincides with the corresponding ultrasonic data [5]. This strongly suggested, at the time, that both the electromagnetic and acoustic anomalies had the same origin. That the coincidence is not purely circumstantial was shown soon afterwards in a number of elegant electro-acoustic experiments: increasing the AC electromagnetic field leads to saturation of the structural transitions and a decrease in ultrasonic attenuation [37, 38]. In addition, exposure to the AC field affects the *acoustic* impedance of a glass [38]. Again, the sufficient sensitivity of these experiments is due to the interaction with the AC field being resonant. Finally we mention yet another venue in investigating the TLS coupling to electric fields, namely the electric dipolar echo, see e.g. [32, 39].

The dipole moment magnitudes, reported in all these experiments on the respective substances, are all of the

order 1 Debye, although more recent measurements seem to be converging on a fraction of a Debye. Unfortunately, the extracted dipole values do not completely agree between different experiments. So, for example, Kharlamov *et al.* [40] give relatively low values of 0.2 and 0.1 D for PMMA and PS, respectively, based on their field induced spectral diffusion data. The degree of the quantitative discrepancy is, of course, subject to the detailed assumptions on the distribution of the individual TLS parameters, various angular averagings etc.

3. Dipole–dipole interaction

The idea of local structural transitions is internally consistent in that the transitions are indeed distinct, weakly interacting entities. This is easy to understand by considering the moment of vitrification, when a particular pattern of mobile regions sets in: a transition will be found locally, upon freezing, if at T_{g} it was of marginal stability with respect to external mechanical perturbation, as delivered by stress waves to the given local region. It does not matter, of course, whether the source of these waves is thermal elastic fluctuations or the other structural transitions. Now, upon having estimated the energy spectrum of the TLS and their coupling to the phonons [17], one may check the magnitude of the resultant TLS–TLS interaction, mediated by the acoustic waves in the frozen lattice. Such interaction self-consistently turns out to be small [20]. We are aware of several observable consequences of the interaction. For one thing, this interaction tends to quench the spontaneous echo generation [7, 33], by virtue of dephasing each TLS’s motion when the TLS precesses about its local field. Another, remarkable effect from the interaction is that it gives rise to a negative thermal expansion coefficient in some glasses, at low enough temperatures [20]: the fluctuating entities in the lattice attract in the van der Waals fashion, via exchanging phonons. This attraction, counterbalanced by the material’s stiffness, acts to partially contract the sample. The number of thermally excited transitions increases with the temperature and thereby enhances the degree of contraction. The effect is small, about 10^{-6} , but nevertheless observable. The often employed dimensionless parameter characterizing lattice non-linearity—the Grüneisen parameter—is usually positive and of the order unity in crystals. It was found to be large and negative in many glasses at cryogenic temperatures, see e.g. [41].

The direct phonon mediated TLS–TLS interaction goes as $1/r^3$, just like the usual dipole–dipole interaction, but is somewhat complicated by the tensorial form of

the coupling (see e.g. [33] for a discussion). If, however, the transverse and longitudinal speeds of sound were equal, the interaction would be strictly dipole–dipole. It is therefore often convenient to assume the elastic interaction is indeed purely dipole–dipole resulting in a small *quantitative* error. With this simplification, a ‘scalar’ phononic Hamiltonian can be used: $\frac{1}{2}\lambda_{ij,kl}\phi_{ij}\phi_{kl} \rightarrow \frac{1}{2}\rho c_s^2(\nabla\phi)^2$, where ϕ is a scalar displacement field polarized in a single direction. The coupling will become $g_{ij}\phi_{ij}\sigma_z \rightarrow (\mathbf{g}\nabla\phi)\sigma_z$. (The tensorial character of the interaction may actually be important in the Grüneisen parameter context, see [20] and below). The presence of an electric component to each transition dipole moment clearly leads to another contribution to the total interaction. Since a detailed discussion of the interaction effects has already been given elsewhere [20], here we simply estimate the strength of the electric dipole–dipole coupling relative to the purely elastic counterpart and the rest follows in a straightforward fashion.

The elastic dipole–dipole interaction is given by a simple formula, see e.g. [10, 20]:

$$\mathcal{H}_{\text{elast}} \simeq \frac{g^2}{\rho c_s^2} \frac{1}{r^3} \simeq T_g \left(\frac{a}{r}\right)^3, \quad (21)$$

where, for the sake of clarity, we eschew some numerical constants (these could be found in [20]) and have used equation (17). The electric dipole–dipole interaction, by equations (12) and (19), is, on the other hand,

$$\mathcal{H}_{\text{elect}} \simeq \zeta^2 \rho c_s^2 a^3 \left(\frac{a}{r}\right)^3. \quad (22)$$

What is the relative value of the two interactions? A useful rule of thumb is that $g \simeq (T_g \rho c_s^2 a^3)^{1/2}$ is of the order eV for all substances. In silica, for instance, $\rho c_s^2 a^3$ is several eV, the Rydberg scale being a convenient (and physically justified) landmark. The T_g of silica is 1500 K, i.e. slightly larger than 0.1 eV. We therefore make an interesting observation that the electric dipole–dipole interaction *can* be comparable in magnitude to the elastic counterpart for polar enough substances. This is despite the relatively weak contribution (1% or less) of the Coulombic forces to the apparent mechanical stiffness. We will speculate on the physical significance of this observation in the final section of the article, while for now, we limit ourselves to a formal notion: the elastic dipole–dipole interaction is disadvantaged, compared to the electric counterpart, due to the large ρc_s^2 term in the denominator of equation (21): phonons are not true gauge particles.

Leggett has emphasized [42] that the dimensionless Grüneisen parameter varies ‘wildly’ between different amorphous substances, in contrast with the nearly universal l_{mfp}/λ ratio. Lubchenko and Wolynes have argued [20] this stems from the van der Waals attraction between the tunnelling centres, which is strongly enhanced by ‘Boson peak’ excitations. The total attractive interaction consists of several contributions, is temperature dependent, and is expressed in terms of various combinations of the temperature, T_g and the Debye temperature. While it may be argued that there is an intrinsic *upper bound* on the value of ζ (see below), there otherwise seems to be little intrinsic connection between the polar and structural characteristics of glasses, in general. As a result, the electrostatic interaction from equation (22) is expected also to contribute to the non-universality of the Grüneisen parameter. This notion is consistent with the sensitivity of the Grüneisen parameter in silica to the concentration of polar impurities [41]. Further, the magnitude of the negative thermal expansivity is indeed larger in more polar mixtures according to [41].

3.1. Symmetry versus transient piezoelectricity

We have so far focused on the dipole moment of one of the structural states *relative* to the other, namely $\sum_i \Delta\mu_i = \mu_T$, since it is what determines the coupling of the transition to the external field. We next inquire whether there is a correlation between the degree of polarity of a state with its absolute energy. For example, suppose for a moment that the lower energy state is completely non-polar, so that the two-level system dipole moment is completely due to the excited state. Such a situation could be exploited experimentally: one could supercool a liquid just enough so that it does not crystallize readily (the way glassblowers do), then expose the sample to a strong electric field for a sufficient while, and then quench the sample below its T_g . After that, remove the field. Clearly, the number of dipole moments along and opposite to the field direction will differ. In other words, a number of dipoles will be actually lined up in a preferred direction, leading to a (weak) ferroelectric order. As a consequence of this, removal of the field in the procedure above should lead to the sample’s contraction (which is the sample’s way of minimizing the ferroelectric energy). Some residual polarization will appear as well. If the field is removed sufficiently fast, the sample will also heat up some. (This, in a sense, represents an antithesis to adiabatic demagnetization). Such polarization will not take place if the degree of polarity is uncorrelated with the energy of a structural state, at least within the relevant energy range. Conversely, since this relevant energy range (1 K or less)

is quite small relative to the glass transition temperature, anisotropy effects, if any, are expected to be small. (See a related discussion of the Phillips' thermal contraction mechanism in [20]).

While we cannot, at present, rule out *a priori* the 'pyroelectric' scenario above, it seems rather unlikely for the following reason. An amorphous sample, at least at long enough times, should have inversion symmetry, on average. With this symmetry present, no piezoelectricity, let alone pyroelectricity, can take place [26]. The question therefore is whether an external field breaks the inversion symmetry (locally) without inducing crystallization. Perhaps it will, on short enough time scales, before considerable aging takes place. An experimental study would settle this issue. At any rate, even if present, ferroelectric order would not affect the thermal expansion properties at low temperatures (cf. the discussion of the Grüneisen parameter in [20]). This attraction mechanism is temperature independent and simply contributes to the effective molecular field at each TLS site.

4. Closing remarks

In this article, we have outlined the microscopic origin of the coupling of the intrinsic structural transitions in amorphous solids to electric fields. The coupling stems from rotation of the molecular bonds, within the region encompassing the transition, which generates a net electric dipole. The molecular constituents of a glass, even if intrinsically non-polar, are strained due to disorder. Therefore, small partial charges on each atom are expected leading to the presence of electric dipole moments associated with individual bonds.

A local structural transition occurs by moving a domain wall through the region. The domain wall is a mechanically strained region separating alternative structural states. Such strained regions are frozen-in thermal fluctuations of the lattice. (Above T_g , the lifetime of such a frozen-in structure would not exceed the typical α -relaxation time in the liquid). In an analogous fashion, the dipole moment can be thought of as frozen-in polarization fluctuations, or as the local piezoelectric response to local strains.

The glass transition is driven by steric, i.e. mechanical interactions, not primarily by electrical ones, which is reflected in the smallness of the partial charge *on a bead*, given in the theory by the dimensionless quantity ζ . So, for example, the elastic modulus can be represented as $\rho c_s^2(1 + \zeta^2)$, where $\zeta^2 \lesssim 0.01$ is the contribution of the ionic forces to the overall material stiffness. (Here, we discriminate between ionic (or hydrogen) bonds, as in NaCl or H₂O, and covalent bonds, as in diamond).

In spite of its apparent small contribution to the material's structural integrity, the Coulomb component could actually be comparable to the elastic component of the interaction between distinct *transitions*. Note such interactions are unimportant as far as the identity of each transition is concerned, because the corresponding regions are statistically far apart [20]. Nevertheless, this weak interaction may be viewed, loosely, as the successful attempt of the system to have avoided entropically costly local ferroelastic order. With this in mind, and the relatively strong Coulomb interaction of structural fluctuations, the apparent smallness of the partial charges on a bead bears the following consequences: the glassforming ability of a mixture of ionic components crucially depends on their mutual stoichiometry. There has to be a way to make a weakly charged bead out of the strongly charged atoms. (We remind the reader that a bead usually consists of *several* atoms). This in fact is realized in amorphous silica, germania, or zinc dichloride, where the cation is surrounded by four anions, in a nearly tetrahedral fashion. The tetrahedra are known to be quite rigid and move as a whole during transitions (see e.g. [43]). As a result, the glass bead must be a significant fraction, volumetrically, of the tetrahedron. Note that the estimates of the bead volume by Lubchenko and Wolynes in [15, 17], which turns out to be about a half of that of the SiO₄ unit, reproduce the experimental heat capacity and are indeed consistent with the bead being only slightly charged. On the other hand, an arrangement that minimizes a bead charge is difficult to achieve in equi-valent mixtures, such as NaCl, or water, because of the strong anisotropy of the hydrogen bond. These materials do not vitrify readily but instead, form low density lattices. (Note, ice does amorphize under high pressure, see e.g. [44]). To summarize, the requirement of the amorphous lattice stability, with respect to purely Coulombic interactions, imposes an upper bound on the ζ^2 value.

Consider now equation (11). In order for the lattice to be stable, the λ' matrix (with an ij pair considered a single index) should be positive definite. This means, if a particular λ is negative, the corresponding β could be, in principle, quite large. This would imply large induced dipole moments. As just argued, the Coulomb component is likely to be small in a glass, because the latter is rather homogeneous. Defects in crystals, however, can be more extended and can be highly anisotropic. In this regard, we wish to mention the single chromophore studies of spectral drift in a Shpolskii matrix, by Bauer and Kador [45]. These authors have seen a transition (presumably due to a structural defect) that generated a remarkably large dipole moment of 8 Debye. Note, the Shpolskii matrix is polycrystalline, not strictly amorphous.

Finally, we remark there is more to electrodynamics of amorphous solids than what could realistically be discussed in this article. Here, we have analysed only the case of good electric insulators. Distinct, interesting phenomena take place in semiconductors and metallic glasses. As an example, let us mention an old experiment of Claytor and Sladek [46], who found enhanced ultrasonic attenuation in As_2S_3 glass upon removal of electric field. This extra attenuation was greatly reduced by infrared radiation, which suggested that there is, we quote, ‘atomic relaxation accompanying electronic transition in gap states where injected carriers have been trapped’. We leave this for future work.

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