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The relation between stretched-exponential relaxation and the vibrational density of states in glassy disordered systems

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ABSTRACT

Amorphous solids or glasses are known to exhibit stretched-exponential decay over broad time intervals in several of their macroscopic observables: intermediate scattering function, dielectric relaxation modulus, time-elastic modulus, etc. This behaviour is prominent especially near the glass transition. In this Letter we show, on the example of dielectric relaxation, that stretched-exponential relaxation is intimately related to the peculiar lattice dynamics of glasses. By reformulating the Lorentz model of dielectric matter in a more general form, we express the dielectric response as a function of the vibrational density of states (DOS) for a random assembly of spherical particles interacting harmonically with their nearest-neighbours. Surprisingly we find that near the glass transition for this system (which coincides with the Maxwell rigidity transition), the dielectric relaxation is perfectly consistent with stretched-exponential behaviour with Kohlrausch exponents $0.56 < \beta < 0.65$, which is the range where exponents are measured in most experimental systems. Crucially, the root cause of stretched-exponential relaxation can be traced back to soft modes (boson-peak) in the DOS.

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1. Introduction

Since its first observation by Kohlrausch in 1847 [1], stretched-exponential relaxation has been observed in the time-dependent relaxation of several (elastic, dielectric, electronic) macroscopic observables in nearly all structurally disordered solids. Ultimately, this behaviour represents one of the most common hallmarks of irreversibility in disordered systems. Over the last century, stretched-exponentials have been used in countless experimental settings to fit experimental data. Although it is common knowledge that stretched-exponential relaxation relates somehow to spatially heterogeneous many-body interactions or to heterogeneous distribution of activation energy barriers [2,3], only very few models or theories are able to predict stretched-exponential relaxation from first-principle dynamics [4]. In fact, strictly speaking, only two models recover stretched-exponential relaxation in well-defined specific situations. One is a model of electronic relaxation via non-radiative exciton-hole recombination where holes are randomly distributed traps that “eat up” the diffusing excitons [5–7]. As shown in Ref. [7], according to this model the density of not-yet trapped excitons decays at long times as $\sim \exp(-t^{d/d+2})$,

which gives a Kohlrausch exponent $\beta = 0.6$ in 3d. In spite of the elegance of this model, it is not straightforward to apply it to elucidate Kohlrausch relaxation in glasses. The other model is the Mode-Coupling Theory (MCT) of supercooled liquids, which gives a solution that can be approximated with a stretched-exponential for the intermediate scattering function at temperatures well above the glass transition [8–10].

Clearly, these two models are quite specific and limited in their applicability [11,12]. For example, starting with Kohlrausch original experiment using the Leyden glass jar, most of the physical systems where stretched-exponential behaviour has been observed are represented by disordered solids, well below the glass transition where MCT is no longer applicable. This is a very important topic in electrical engineering, where dielectric insulators in the solid state are typically employed for all high-voltage transmission applications [13].

Hence, while stretched-exponential relaxation is ubiquitous in the solid-state, it has not been possible to trace it back to a well-defined mechanism in the many-body dynamics, or to a well-defined microscopic descriptor of the dynamics. In this Letter, we re-examine the problem from the point of view of lattice dynamics, suitably evaluated for a model of disordered solids. Focusing on the paradigmatic case of dielectric relaxation, it is shown that stretched-exponential decay of the dielectric modulus over many

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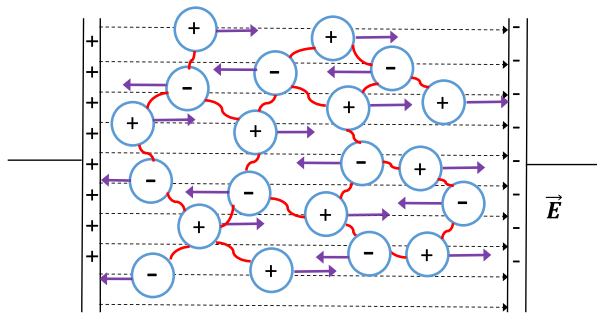


Fig. 1. Goldhaber–Teller model of a disordered dielectric solid. Spherical particles with positive and negative charge (or equivalently, neutral) are inter-dispersed randomly. Each particle interacts with its nearest-neighbours (which bear opposite charge) uniquely via an attractive harmonic potential (linear springs, in red). Note that the charges do not contribute explicitly to the harmonic inter-particle interaction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

decades in time is recovered by the numerical solution to the Lorentz sum-rule with a DOS that takes into account the crucial role of so-called boson-peak modes over the Debye $\sim \omega_p^2$ law. Since the origin of these modes lies in the Ioffe–Regel crossover [14–17] at which phonons are scattered off by the disorder (in particular, by the absence of inversion-symmetry of the lattice [18]), it is possible to establish a direct link between stretched-exponential relaxation and the quasi-localization of phonons by the disorder at the boson peak.

2. Goldhaber–Teller model of disordered dielectric

In the following, we work within the assumption of disordered elastically bound classical charges, which is the same as the Goldhaber–Teller model originally developed to explain the giant dipole resonance in atomic nuclei [19,20]. In this model, schematically depicted in Fig. 1, two types of charges, positive and negative (or, equivalently, positive and neutral, as in the Goldhaber–Teller model for nuclei), are inter-dispersed randomly in space. Every positive charge is surrounded by nearest-neighbours (which are negative, or neutral), to each of which it is bound by an attractive harmonic potential. In a dielectric solid or in a supercooled ionic liquid [21], an attraction minimum around which harmonic approximation can be taken, may come from a superposition of electrostatic attraction and van der Waals attraction, competing with short-range steric repulsion (while in the original Goldhaber–Teller model the attraction comes, evidently, from the strong nuclear force).

In order to evaluate the dielectric response (below) on the basis of lattice dynamics, we make use of a DOS $\rho(\omega_p)$ obtained by numerical diagonalization of a model random lattice of harmonically-bound spherical particles. This random network is obtained by driving a dense Lennard–Jones liquid into a metastable glassy energy minimum with a Monte–Carlo relaxation algorithm, and then replacing all the nearest-neighbour pairs with harmonic springs all of the same spring constant, and with a relatively narrow spring-length distribution [18]. Springs are then cut at random in the lattice to generate random lattices with variable mean coordination Z , from $Z = 9$ down to the isostatic Maxwell limit $Z = 2d = 6$. It is important to notice that this simplified model DOS is applicable only to systems where the building blocks are spherical and interact with central-force potentials. The DOS obtained from numerical diagonalization of the simulated network is expressed in terms of dimensionless eigenfrequencies ω_p .

In this random assembly of particles, only nearest-neighbour interactions are present, and the number Z represents the average coordination number or average number of nearest-neighbours per

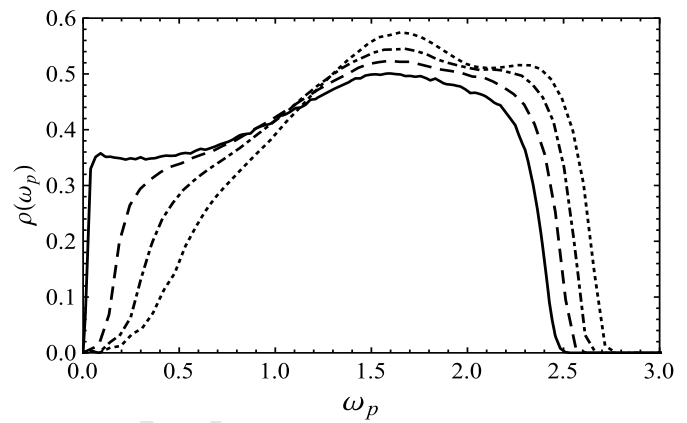


Fig. 2. Density of states (DOS) with respect to eigenfrequency ω_p at $Z = 6.1$, i.e. close to the marginal stability limit $Z = 6$ that we identify here as the solid–liquid (glass) transition, $Z = 7$, $Z = 8$, $Z = 9$, which are marked as solid, dashed, dotted and dotted lines respectively.

particle. Also, the DOS obtained from diagonalization of the model random networks, depends sensitively on the average coordination number Z . For example, the boson peak frequency drifts towards lower values of ω_p upon increasing Z , according to the scaling $\omega_p^{BP} \sim (Z - 6)$, as observed also in random packings [23]. This behaviour is also consistent with the common observation that in glasses the boson peak frequency shifts to lower frequency upon increasing the density or the pressure [24]. Hence, Z is the crucial control parameter of the relaxation process, which, in a real e.g. molecular glass, changes with T . Therefore, in order to use our numerical DOS data in the evaluation of the dielectric function, we need to find a physically meaningful relation between Z and T at the glass transition.

In all experimental systems which measure the T -dependent material response, the temperature is varied at constant pressure, which implies that thermal expansion is important. Following previous work, we thus employ thermal expansion ideas [25] to relate Z and T . Upon introducing the thermal expansion coefficient $\alpha_T = \frac{1}{V}(\partial V/\partial T)$ and replacing the total volume V of the sample via the volume fraction $\phi = vN/V$ occupied by the molecules (v is the volume of one molecule), upon integration we obtain $\ln(1/\phi) = \alpha_T T + \text{const}$. Approximating $Z \sim \phi$ locally, we get $Z = Z_0 e^{-\alpha_T T}$. Imposing that $Z_0 = 12$, as for FCC crystals at $T = 0$ in accordance with Nernst third-law principle, we finally get, for the example of glycerol, $Z \approx 6.02$ when $T = 184$ K. This is very close to the reported T_g for this material [22]. For $Z = 7, 8$ and 9 , the corresponding temperatures are calculated to be $T = 144$ K, 108 K and 77 K.

It is seen in Fig. 2 that for the case $Z = 6.1$, i.e. very close to the solid–liquid rigidity transition that occurs at $Z = 6$, a strong boson peak is present in the DOS. The continuum Debye regime $\sim \omega_p^2$ is not visible or absent, whereas an infinitesimal gap between $\omega_p = 0$ and the lowest eigenfrequency exists. Hence, under conditions close to the glass transition, the vibrational spectrum is dominated by soft modes at low frequency. Upon increasing Z , the extent of soft modes at low frequency decreases markedly while the Debye $\sim \omega_p^2$ regime extends to higher frequencies. At the highest Z values, the relics of van Hove singularities that characterize FCC crystals become visible, because medium-range order has to increase upon increasing the coordination Z [18], towards the FCC limit $Z = 12$. In particular, the local degree of centrosymmetry of the nearest-neighbours is the crucial form of order which increases upon increasing Z and correlates directly with the boson peak [18]. Note that $Z_0 = 12$ for FCC is independent of density only if the thermal fluctuations are neglected (as is the case at $T = 0$ or for athermal systems, e.g. hard spheres). At a finite T , defects

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