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## LETTER TO THE EDITOR

# Random energies, random coordination numbers, the Vogel–Fulcher law, and non-exponential relaxation

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**Abstract.** The collective dynamics of particles in random energies and with a narrow distributed random coordination number shows a dynamical transition. The characteristic macroscopic time scale averaged over the coordination number and the energy distribution diverges with an essential singularity, i.e. as the celebrated Vogel–Fulcher law which is widely used in the treatment of experimental data for the viscosity and relaxation times of glass forming liquids.

The dynamics of particles near the glass transition of a fluid is extremely slow. This is similar to any phase change, where, when approaching a critical temperature  $T_c$  the characteristic time scale diverges as a power law of the form (critical slowing down) [1]

$$\tau \sim \xi^z \sim (T - T_c)^{-\nu z} \quad (1)$$

where  $\xi$  is the correlation length,  $\nu$  is the correlation length exponent, defined by

$$\xi \sim (T - T_c)^{-\nu} \quad (2)$$

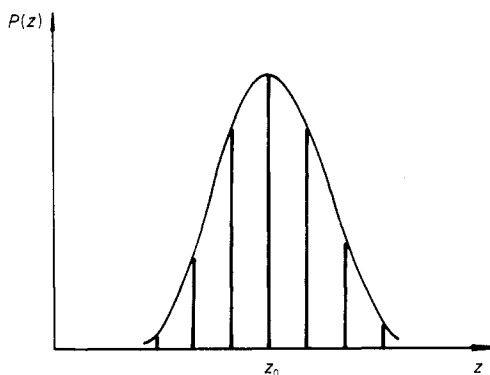
and  $z$  is the dynamic exponent.

Such a dynamical scaling analysis is only possible for pure equilibrium phase transitions. Freezing transitions or glass transitions belong to the class of non-equilibrium phase changes, and if power laws, such as given in (1), are applied to real values for the relaxation time  $\tau$  in a glass transition or spin glass transition the exponent  $z\nu$  turns out to be unusually large [2]. An empirical formula for the characteristic macroscopic time scale has been suggested a long time ago by Vogel and Fulcher (see [3]), i.e.

$$\tau \sim \exp(A/(T - T_0)) \quad (3)$$

which diverges more strongly than any power law as given in (1).  $T_0$  is a temperature lower than the glass transition temperature [4]. Many experimental data have been fitted with success to this law [4, 5].

From a theoretical point of view it has been found difficult to derive the Vogel–Fulcher law from a simple physical picture [6], but progress has been made and it was shown that the essential singularity appearing in the Vogel–Fulcher law is connected to cooperative motions [7–10]. This has been demonstrated explicitly in a model consisting of stiff polymeric rods. The number of rods which participate in a well defined manner



**Figure 1.** The discrete distribution is approximated by a Gaussian around the most probable coordination number  $z_0$  with the appropriate width.

in a cooperative motion diverges with a power law if the freezing transition, which produced the Vogel–Fulcher law, is approached [7, 8].

In this letter we show that such behaviour can be very general, and the Vogel–Fulcher law can be derived by simple arguments. We need four basic facts from the physics of the condensed glassy phase and the glass transition phenomenon, which are listed in the following.

(i) The characteristic time scale for the simple hopping of an arbitrarily chosen test particle out of an energy valley with depth  $E$  is given by the Arrhenius law

$$\tau(E) \sim \exp(\beta E) \quad (4a)$$

where  $\beta$  is the inverse temperature, i.e.  $\beta = 1/T$  (here units with the Boltzmann constant  $k_B = 1$  are chosen).

(ii) The energy barrier  $E$  depends on the number of particles which surround the test particle, i.e. if the particle is in an environment of  $z$  particles which form a cage, it is easier for the particle to jump out of this cage than, for example, from another one where it is surrounded by  $z + 1$  particles. Thus we have

$$\tau \sim \exp(\beta E(z)). \quad (4b)$$

For simplicity we assume in the following  $E(z) = zE$ , i.e. a linear relationship for the energy and the coordination number [10].

(iii) It is known that the coordination number in amorphous systems is not a fixed quantity and varies from place to place [11]. It is itself a random number. The distribution around some mean value  $z_0$  has a very narrow width. We assume here (for simplicity) a Gaussian distribution for the coordination number, i.e.

$$P(z) = [1/2\pi(\Delta z)^2]^{1/2} \exp[-(z - z_0)^2/2(\Delta z)^2]. \quad (5)$$

This distribution is an approximation and the result of the central limit theorem. An example for a real distribution would be discrete and is sketched in figure 1. It is sharply peaked around the most probable coordination number  $z_0$ . The width  $\Delta z$  is of the order of 1–5 particles and the mean value of  $z_0$  is of the order of 14 in three dimensions [11].

(iv) The energy  $E$  itself is a random number in amorphous systems, such as glasses and spin glasses. The phase space can be visualised as an irregular many-valley picture [12]. The energies are random and for simplicity we assume Gaussian distributed, i.e.

$$P(E) = (1/2\pi E_0^2)^{1/2} \exp(-E^2/2E_0^2). \tag{6}$$

This is similar to the random energy model [13].

The characteristic time scale, which is relevant for macroscopic purposes is the average

$$\tau(\beta) = \langle \tau(z, E) \rangle = \int_{0 \leq z \leq \infty} dP(z) \int_{-\infty \leq E \leq \infty} dP(E) \exp(\beta z E). \tag{7}$$

The average over the energies can be done analytically, while the exact average over the coordination number leads to an error function, since the integration range is limited by 0 as a lower bound. If we extend the coordination number formally to infinity we make a slight mistake. But we note that the error which is made by extending the integration limit to  $-\infty < z < \infty$  is small, since the distribution of the coordination number is sharply peaked around  $z_0$ . The assumption that the coordination number is infinite is crude but in terms of the cooperativity which is present in glass forming systems, we know that a lot of particles have to be moved before one special particle can move [7, 8]. Then we approximate the distribution function of the coordination number by a Gaussian of the appropriate width in order to carry out the calculation analytically. For other distributions, numerical computations have to be done. But it has to be remembered that the use of a Gaussian is a crude model. Thus we have

$$\tau(\beta) \approx \int_{-\infty}^{\infty} dz P(z) \int_{-\infty}^{\infty} dE P(E) \exp(\beta z E). \tag{7a}$$

The integrals converge for temperatures which satisfy  $1 - \beta E_0 \Delta z > 0$  and the final result is

$$\tau(\beta) = \exp\{\beta^2 z_0^2 E_0^2 / 2 [1 - E_0^2 (\Delta z)^2 \beta^2] - \frac{1}{2} \log [1 - \beta^2 E_0^2 (\Delta z)^2]\}. \tag{8}$$

The second term in the exponential can be neglected near the dynamical transition. Equation (8) can then be rewritten as

$$\tau(T) \approx \exp\{[(z_0/T)^2 E_0^2 / 2] / (1 - \Delta z E_0 / T)(1 + \Delta z E_0 / T)\}. \tag{9}$$

With the definition  $T_0 = \Delta z E_0$  and the approximation  $1 + T_0/T \approx 2$  near the transition at  $T = T_0$ , we find the Vogel–Fulcher law for the relevant time scale

$$\tau(T) \sim \exp[(z_0 / (2\Delta z)^2) / (1 - T_0/T)]. \tag{10}$$

Note that the transition  $\tau \rightarrow \infty$  comes at  $T_0 = \Delta z E_0$ , i.e. the critical temperature is given by the fluctuation of the coordination number  $\Delta z$ , which is present *and* characteristic only in amorphous systems. Note that the essential singularity is a result of the fact that we took the coordination number to infinity. If we had avoided this, we would find no singularity as in Bässler’s work [14] and we would have to define the glass transition where the relaxation time exceeds a certain value. The result of Bässler will be reviewed below in this letter.

To summarise we note that two stochastic quantities in random systems, i.e. the energy and the coordination number are responsible for the appearance of the Vogel–Fulcher law, which shows an unusual essential singularity. A special case of this has been

discussed recently by Bässler [14] and by the present author [9]. (This is also contained in our simple but more general discussion.) There it was considered that the energy is random and has a Gaussian distribution but the effect of the fluctuating coordination number has been ignored. This case corresponds to our general formula, if we put  $\Delta z = 0$  in (8), i.e. the coordination number is fixed and does not fluctuate. The result is then

$$\tau(T) \sim \exp[(T'_0/T)^2] \quad (11)$$

with  $T'_0 = z_0 E_0$  which is the result of Bässler [9, 14]. Note that a dynamical transition in this model at finite temperatures is not present. Such a system freezes at  $T = 0$ . As noted above the transition can be defined where the relaxation time (or the viscosity, which is proportional to the relaxation time) reaches a certain value, i.e. if the viscosity is larger than  $10^{13}$  P, if this model is applied to the glassy transition.

Another interesting question is the macroscopic relaxation function  $\varphi(t)$  in the context of this random energy and random coordination number model.  $\varphi(t)$  can be defined as follows. Suppose that each of the jumps out of a valley with depth  $E(z) = Ez$  corresponds to a Debye subrelaxation function of the form  $\varphi(t, E, z) \sim \exp[-t/\tau(E, z)]$  and the macroscopic one is the averaged relaxation function, i.e.

$$\varphi(t) \sim \langle \exp[-t/\tau(E, z)] \rangle. \quad (12)$$

The averages are not simple to calculate and only asymptotic expressions can be given. The integrals, which occur in the averaging calculation are of the form

$$f(t) = \int du \exp(-t \exp(-\beta u) - \alpha u^2) \quad (13)$$

which cannot be calculated analytically, but one can parameterise the  $\exp(-u^2)$  by 'uncompleting the square', i.e.

$$\exp(-u^2) = \int d\psi \exp(2i\psi u - \psi^2). \quad (14)$$

The integration is then possible and in the limit of large times  $t \rightarrow \infty$ , we find the relaxation function to be

$$\varphi(t) \sim t^{-T/\Delta z E_0} \exp(-\log^2 t^{T/z_0 E_0}). \quad (15)$$

Note that the decay in this relaxation function is stronger than the power law but broader than the single exponential decay. Similar relaxation functions have been found previously in the context of hierarchical relaxation [14–16], in one-dimensional models [17], and in models with pure energy disorder [18]. More details will be given in an extended paper.

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