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Scenario for the Vogel-Fulcher "law"

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A scenario is presented to explain the Vogel-Fulcher "law" which describes the slowing down of relaxation processes associated with many glasses: $\tau^{-1}=\tau_0^{-1}\exp[-E/(T-T_0)]$. It assumes that relaxation processes are local and satisfy an Arhennius law whose activation energy E_a is determined by the energy needed to jump out of a local potential well. This latter is determined by employing a local Landau expansion of the free energy in powers of the order parameter, where it is assumed that frustration and quenched-in randomness lead to local order which is incompatible with global order. In the free energy, the randomness is considered to provide a linear coupling which drives the quadratic term, with the quartic term preventing the divergence at T_0 from actually occurring.

A scenario is presented for a derivation of the Vogel-Fulcher (VF) "law" for the slowing down of relaxation processes that is found in many glasses. The associated relaxation time τ has been found to take approximately the form[1-5]

$$\tau^{-1}=\tau_0^{-1}\exp[-E/(T-T_0)]\,, \tag{1}$$

where E is an energy, τ_0^{-1} is a microscopic attempt rate, and T_0 is an ordering temperature whose significance has remained unclear. [In practice, (1) holds only for temperatures somewhat above T_0; the singularity is not actually observed.[3]] The scenario has the merits that it is transparent, it introduces no new physical principles, and it has enough freedom to treat the case of glasses for which VF does not hold. In its current form, there is no microscopic prescription to calculate its parameters, although we present two possible physical pictures which may underly the model.

The central motivation for this work was to find a general framework whereby the characteristic activation energy E_a in an Arrhenius law,

$$\tau^{-1}=\tau_0^{-1}\exp(-E_a/T)\ ,$$

could appear to vary as $(T-T_0)^{-1}$ as the temperature T_0 is approached. As will be shown, this can be easily done by taking a standard Landau free energy (for an unspecified order parameter), with the addition of a linear coupling to a local random field. It is somewhat like the problem of a ferromagnet above its Curie temperature T_C, subject to locally random but fixed magnetic fields. In that case, the local susceptibility diverges as one approaches T_C, and the system locally polarizes, with a local decrease in free energy proportional to $(T-T_c)^{-1}$. For the system to order as a whole, it must raise its energy out of its local wells in order to then enter a common ordered well. Thus, the characteristic local well energy provides an energy barrier which is responsible for making the ordering process more difficult to occur, and is the characteristic energy which determines relaxation processes. The case of glasses differs from the case of ferromagnets with random fields in that frustration effects prevent a common global order from occurring. The mathematical framework, being simple and "robust", may have greater validity than the specific physical picture to be presented afterward.

We assume a simple form for the free energy F:

$$F=\tfrac{1}{2}a(T-T_0)x^2+\tfrac{1}{3}bx^3+\tfrac{1}{4}cx^4-hx\ , \tag{2}$$

where a, b, c, T_0 are unspecified constants, h is a spatially varying local field, and x is the order parameter. This is intended to describe a local region of dimension l. In the absence of the local field h, the system would have a first-order transition at $T_1=T_0+\alpha b^2/ac$, where α is of order unity. However, adding the local field leads to a situation where the local field "seeds" a local order which is different in different regions, even above T_0. (In principle, the local field h should be history dependent, but we will neglect such considerations.) Thus, the random fields suppress the transition at T_1, and for that reason we will drop the term in b.

Following the above discussion, we assume that, for one region to have its order parameter change to a value which is more compatible with that in a neighboring region, it must undergo a fluctuation over a barrier determined by F. (Note that we have not explicitly specified a term in the free energy which would make it energetically favorable to do this; if it is not large then it would not affect the present argument.) It will be seen that this barrier can vary as $(T-T_0)^{-1}$ over a wide range in temperature, but the singularity at T_0 never occurs; this would explain why it has been so difficult to make detailed experimental statements about the nature of the transition.

Minimization of (2), with b set to zero, leads to

$$0=\frac{\partial F}{\partial x}=a(T-T_0)x+cx^3-h\ , \tag{3}$$

which has only one real root for $T>T_0$, given by

$$x=x_0(A-B)\,. \tag{4}$$

Here

$$x_0 \equiv (h/c)^{1/3}, \tag{5}$$

$$A = \{\tfrac{1}{2}[(1+r\epsilon^3)^{1/2}+1]\}^{1/3}, \tag{6}$$

$$B = \{\tfrac{1}{2}[(1+r\epsilon^3)^{1/2}-1]\}^{1/3}, \tag{7}$$

and

$$\epsilon = \frac{T-T_0}{T_0} \tag{8}$$

is the reduced temperature. The parameter

$$r = \frac{4}{27}\frac{(aT_0)^3}{h^2 c} \tag{9}$$

gives a measure of the tendency to satisfy the VF law (which, as indicated above, is not satisfied by all glasses[3]). Placing (5) into (2) yields

$$\frac{F}{F_0} = \frac{3}{2^{5/3}}(r^{1/3}\epsilon)(A-B)^2 + \tfrac{1}{4}(A-B)^4 - (A-B), \tag{10}$$

$$F_0 \equiv (h^4/c)^{1/3}. \tag{11}$$

For $\epsilon = 0$ we have $F = -\frac{3}{4}F_0$ and $x = x_0$, as expected.

If the quartic stiffness c, which controls the extent to which saturation effects enter, is small, this favors the VF law, as does having a large local field h. More generally, r of (9) must be sufficiently large if there is to be a large VF regime.

Consider now the limit where $r\epsilon^3 \to \infty$. In that case $x \to h/aT_0\epsilon$, which follows from (3) in the appropriate limits, and thus

$$F \to -\frac{h^2}{2aT_0\epsilon},\quad \frac{F\epsilon}{F_0} \to -\frac{1}{3(2r)^{1/3}}r\epsilon \to \infty. \tag{12}$$

Hence, if F determines the characteristic energy barrier for thermal fluctuations, the constant E that appears in the VF law takes the form

$$E \approx \frac{h^2}{2aT_0^2}. \tag{13}$$

In the above, h must be considered to be a representative value (e.g., the rms value of the local field). For the above description to be valid, E must be of the observed magnitude and (12) must hold in a sufficiently wide temperature range. Numerical evaluation of (10) indicates that (12) is a good approximation from $0.2 < \epsilon < 1$ for $10 \le r$, or from $1 \le \epsilon \le 4$ for $1 \le r$, as can be seen from Fig. 1. $-F/F_0$ and $-\epsilon F/F_0$ are plotted in Fig. 1(a), whereas $-(F/F_0)(T_0/T)$ and $-\epsilon(F/F_0)(T_0/T)$ are plotted in Fig. 1(b).

If E is too small (corresponding to too small a random field h) there will be no VF law. Since annealing can be expected to decrease the random field, one can expect E to decrease and r to increase as the system is annealed.[6] Thus h must be large enough for E of (13) to be sufficiently large, but small enough for r of (9) to be sufficiently large. It is clear, then, that there are ranges of the parameters for which the VF law would not hold, and these ranges occur for entirely different reasons. Let us now consider what experiment might be able to tell us about the parameters of the free energy:

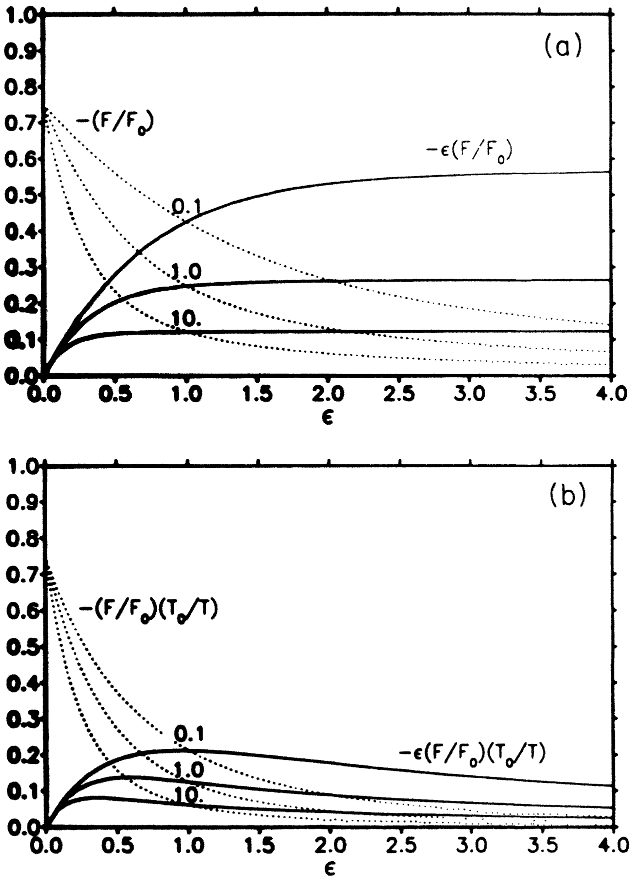

FIG. 1. Part (a) presents both the negative reduced free energy $-F/F_0$ (dotted line) and $-\epsilon F/F_0$ (solid line) as functions of the reduced temperature $\epsilon \equiv (T-T_0)/T_0$, for three values of the parameter r defined in Eq. (9). Part (b) presents $-(F/F_0)(T_0/T)$ (dotted line) and $-\epsilon(F/F_0)(T_0/T)$ (solid line), for the same three values of r.

(1) If a VF law is satisfied, one can directly measure T_0.

(2) If a VF law is satisfied, one can also measure the constant E in (13), thus obtaining the ratio

$$h^2/aT_0 = ET_0. \tag{14}$$

(3) By studying the deviations from VF as one approaches T_0, one can determine r in (9), from which one finds the second ratio

$$h^4/c = \tfrac{27}{4}r(ET_0)^3. \tag{15}$$

If, in addition, one can make a definite identification and measurement of the order parameter x, then the characteristic value x_0 could be determined, leading to a third ratio [cf. (5)]

$$h/c = x_0^3. \tag{16}$$

We now turn to the question of the meaning of the order parameter x. Two possibilities come to mind: an orientational order parameter or a translational order parameter. In either case, the issue of frustration and interaction with the other type of order parameter must be invoked, and for that purpose it will be useful to recall the results of Steinhardt, Nelson, and Ronchetti.[7] These authors studied local bond-orientational order in liquids and glasses, employing purely geometrical considerations, global Landau free-energy considerations, and molecular-dynamics simulations of quench cooling. They found that extended correlations in the (predominantly icosahedral) local orientational order develops in a supercooled Lennard-Jones liquid. It is well known that such orientational order is incompatible with crystalline translational order, and that the presence of either type of order inhibits the growth of the other type. Moreover, for very rapid quench rates, no evidence for long-range orientational order was found.

First consider the case where x would represent an orientational order parameter, presumably of icosahedral symmetry. In principle, icosahedral order could develop in the bulk, leading to a fluid with icosahedral orientational order. However, from Ref. 7 nonuniform orientational order is expected to occur if the system is cooled too quickly. The random field might simply be due to contiguous regions with different quenched-in icosahedral orientations trying to induce a common order.

Now consider the possibility that x is a translational order parameter, such as the order parameter for the state to which the system might ordinarily crystallize. In that case, the random field might be due to the local quenched-in icosahedral order which has frozen in. Since the icosahedral order is incompatible with crystalline order, there is a natural reason to expect that the system will be frustrated in its attempts to crystallize.

To our knowledge, no molecular dynamics studies of model glasses have undertaken to reveal the VF law; on the other hand, studies have been made which yield orientational order in the supercooled liquid state,[7] or permit only orientational order to occur.[8] If one were to make studies that include both translational and orientational degrees of freedom and find the VF law, while monitoring the orientational and translational order (as well as the density, the strains, etc.), then one could test the extent to which a scenario based upon (2) is valid.

It is possible that in glasses the frustration manifests itself on an energy scale so small that Landau free energies are inappropriate; in that case, however, many other works would be called into question. Nevertheless, the VF law is perhaps our strongest hint that something of a collective nature is occuring, and one should therefore take that hint seriously. This suggests that a Landau free energy is indeed relevant. The addition of a random field, frustration, and the Arrhenius activation law, as we have shown, then make it plausible to have a VF "law" to describe thermally activated processes.

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