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Letter to the Editor

The Vogel–Fulcher–Tammann law in the elastic theory of glass transition

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ABSTRACT

We propose that the origin of the Vogel–Fulcher–Tammann law is the increase of the range of elastic interaction between local relaxation events in a liquid. In this picture, we discuss the origin of cooperativity of relaxation, the absence of divergence of relaxation time at a finite temperature and the crossover to a more Arrhenius behavior at low temperature.

The transition of a liquid into a glass on lowering the temperature may appear conceptually simple, yet this phenomenon has turned out to be one of the most difficult and controversial problems in condensed matter physics, the problem of the glass transition [1,2]. At high temperature, relaxation time τ of a liquid follows Arrhenius dependence. On lowering the temperature, τ almost universally deviates from Arrhenius dependence, and follows the Vogel–Fulcher–Tammann (VFT) law:

$$\tau = \tau_0 \exp\left(\frac{A}{T - T_0}\right), \qquad (1)$$

where A and T_0 are constants. The origin of the VFT law is the main open question in the field of the glass transition [1,2].

A related open question follows from the form of the VFT law, namely what happens at T_0. Because τ formally diverges at T_0, several models have suggested that a phase transition from a liquid to a glass phase can exist [1,2]. Because the divergence is not observed in an experiment, it was proposed that the phase transition is avoided due to sluggish dynamics when τ exceeds experimental time scale. However, the nature of the phase transition and the second phase is not clear, which continues to fuel the current debate [1,2]. Interestingly, the VFT law changes to a more Arrhenius form at low temperature, pushing the divergence temperature down [3]. The origin of this crossover is not understood.

Another related problem is the physical origin of 'cooperativity'. The notion of cooperativity of molecular motion, which sets in a liquid as temperature is lowered, was introduced and intensely discussed in several popular theories of the glass transition. These theories are based on the assumption that 'cooperatively rearranging regions', 'domains' or 'clusters' exist in a liquid, in which atoms move in some concerted way that distinguishes these regions from their surroundings [1,2,4–7]. The physical origin of cooperativity is not understood, nor is the nature of concerted motion.

A glass is different from a liquid by virtue of its ability to support shear stress. This suggests that the change of stress relaxation mechanism in a liquid on lowering the temperature is central to the glass transition process, yet stress relaxation is not discussed in popular glass transition theories, including entropy, free-volume, energy landscape and other approaches [2].

In this paper, we discuss how stress relaxation in a liquid changes with temperature. We propose that the origin of the VFT

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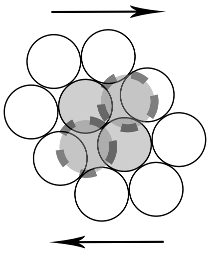

Fig. 1. An example of a concordant local relaxation event. Solid and dashed lines around the shaded atoms correspond to initial and final positions of a rearrangement, respectively. Arrows show the direction of external stress.

law is the increase of the range of elastic interaction between local relaxation events. In this theory, we also discuss the origin of cooperativity of relaxation, the absence of divergence of τ at a finite temperature and the crossover to a more Arrhenius behavior at low temperature.

Relaxation and flow in a liquid proceed by elementary local structural rearrangements, during which atoms jump out of their cages. We call these rearrangements local relaxation events (LREs). Because the divergence of the elastic field due to a LRE is zero, a LRE is not accompanied by compression of the surrounding liquid, and can be viewed, in a simple model, as a pure shear event [2]. Therefore, in discussing how LREs interact elastically, we consider shear LREs. A typical shear relaxation event is shown in Fig. 1 (term 'concordant' in the figure caption is not important here, and will be explained later). The accompanied structural rearrangement produces elastic shear stress which propagates through the system and affects the relaxation of other events. The important question here is how does this stress affect relaxation of other LREs in the liquid?

Lets consider how the changes of stresses due to remote shear LREs affect a given local relaxing region, shown in the center in Fig. 2. Relaxation of the central event involves deformation of the 'cage' around the jumping atom (see Fig. 1), and therefore depends on the stresses that propagate from the remote LREs to the center. A remote shear LRE, similar to the one shown in Fig. 1, creates elastic shear waves, which include waves of high frequency. This is because the deformation, associated with a LRE, creates a wave with a length comparable to interatomic separations (see Fig. 1), and hence with a frequency on the order of the Debye frequency. At high frequency $\omega > 1/\tau$, a liquid supports propagating shear waves [8], which propagate stress and its variations from remote LREs to the central point. If τ is macroscopically defined as the time of decay of shear stress in a liquid [8,9], $d_{\mathrm{el}} = c\tau$ gives the length of this decay, where c is the speed of sound. Here, d_{el} gives an estimation of the maximal range over which shear stress decays in a liquid. At the microscopic level, the relevance of $d_{\mathrm{el}} = c\tau$ is as follows. A high-frequency shear wave originating from a LRE propagates stress until a remote LRE takes place at the front of the wave, at which point the wave front is absorbed by the remote LRE. Suppose this happens at distance d_{el} from the original LRE. d_{el} can be calculated from the condition of equality of the wave travel time, d_{el}/c, and the time at which the remote LRE takes place at point d_{el}. The latter time is given by τ, because microscopically, τ is defined as the average time between two consecutive LREs at one point in space [8], and we obtain $d_{\mathrm{el}} = c\tau$ as before.

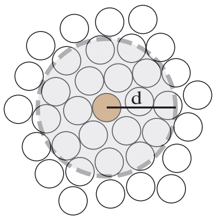

Fig. 2. Illustration of the elastic interaction between local relaxation events. This interaction takes place within the range d_{el} from the central relaxing regions. Shaded and open circles represent local relaxing regions inside and outside, respectively, of the interaction sphere.

Therefore, d_{el} defines the maximal distance over which the central LRE is affected by elastic shear stresses due to other LREs in a liquid (see Fig. 2). For this reason, d_{el} can be called the *liquid elasticity length*. Note that relaxation of the central event is affected by all those stresses that have enough time to propagate to the center. Because it takes time τ for the central event to relax, its relaxation is affected by the stresses from all LREs located distance $c\tau$ away. After time τ, the central event relaxes, and the process repeats. Therefore, the definition $d_{\mathrm{el}} = c\tau$ is self-consistent.

Because c is on the order of a/τ_0, where a is the interatomic separation of about 1 Å and τ_0 the oscillation period, or inverse of Debye frequency ($\tau_0 \approx 0.1$ ps),

$$d_{\mathrm{el}} = c\tau = a\frac{\tau}{\tau_0}, \tag{2}$$

On lowering the temperature, τ increases as $\tau = \tau_0 \exp(V/kT)$, where V is the activation barrier of a LRE [8] (here, V can be temperature-dependent). According to Eq. (2), this increases d_{el} and the number of LREs that elastically interact with a given event. We propose that this is the key to the super-Arrhenius relaxation.

Before discussing the VFT law itself, we note that Eq. (2) immediately gives the crossover from non-cooperative to cooperative relaxation. When, at high temperature, $\tau \approx \tau_0$, $d_{\mathrm{el}} \approx a$ (see Eq. (2)), and $d_{\mathrm{el}} < d_m$, where d_m is the distance between neighboring LREs of about 10 Å (d_m is the distance between the centers of neighboring molecular cages). This means that LREs do not elastically interact. As τ increases on lowering the temperature, $d_{\mathrm{el}} \geqslant d_m$ becomes true. At this point, LREs are no longer independent, because relaxation of a LRE is affected by elastic stresses from other events. This discussion, therefore, clarifies the physical origin of cooperativity. Here, we do not need to assume or postulate cooperativity of relaxation as in the previous work [1,2,4–7]. In this picture, relaxation is 'cooperative' in the general sense that LREs are not independent, but the origin of this cooperativity is the usual elastic interaction. We have recently shown how this interaction gives rise to stretched-exponential relaxation (SER), a universal feature of supercooled liquids [10]. The crossover from exponential relaxation to SER takes place when $d_{\mathrm{el}} = d_m$. According to Eq. (2), τ at the crossover, τ_c, is a universal value: $\tau_c = \tau_0 d_m/a$. This gives τ_c of about 1 ps, consistent with the numerous experiments [11,12].

In order to derive the VFT law, we recall the previous discussion that V is given by the elastic shear energy of a liquid around a LRE [2,13,14]. The energy needed for an atom to escape its cage at the constant volume is very large because of the strong short-range interatomic repulsions, hence it is more energetically favorable for the cage to expand, reducing the energy needed for escape. Such an expansion elastically deforms the surrounding liquid, hence V is given by the work of the elastic force needed to deform the liquid around a LRE. Because this deformation does not result in the compression of the surrounding liquid (for the displacement field $\mathbf{u}$ created by an expanding sphere, $\mathrm{div}(\mathbf{u}) = 0$), V is given by the background shear energy of the liquid. This was confirmed by the experiments showing that V increases with the liquid shear energy [14].

We now recall the previous discussion of how LREs redistribute external stress. In discussing creep, Orowan introduced 'condordant' LREs [15]. A concordant shear LRE is accompanied by a strain in the direction agreeing with the applied external stress, and reduces the local stress and energy (see Fig. 1). In order to counterbalance this decrease, other local regions in a system support more