Elastic models for the non-Arrhenius relaxation time of glass-forming liquids

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One of the mysteries of glass-forming liquids is the almost universally observed deviation from Arrhenius behavior of the viscosity (or average relaxation time). We first briefly review problems with the two traditional approaches to explain this, the free volume model(s) and the Adam-Gibbs configurational entropy model. Attention is then focussed on the "shoving model" [1], according to which the activation energy (the barrier to be overcome for a flow event) is the work performed by the rearranging molecules on their surroundings in order to create some extra space for a short period of time. This work is proportional to the instantaneous shear modulus G_∞, a quantity which is increases with decreasing temperature, and which is much more temperature dependent in glass-forming highly viscous liquids than in other systems of condensed matter physics. The model thus leads to the following expression for the viscosity η as function of temperature T (where V_c is a microscopic volume):

$$\eta(T) = \eta_0 \exp\left(\frac{V_c G_\infty(T)}{k_B T}\right). \qquad (1)$$

We present old and new experimental data supporting the model.

The shoving model provides a connection between fast and slow degrees of freedom. It is thus closely related to several other models which also relate fast and slow degrees of freedom, some of which date back in time to the 1940's and 1950's. Recently there has been a great deal of interest in these sort of connections coming from two important experimental discoveries, both correlating glass properties to the liquid fragility [2, 3]. Adopting a slightly philosophical approach, we shall speculate how these new experiments may relate to elastic models for the non-Arrhenius behavior.

It appears that one can somehow predict the liquid fragility from observations over a very short time. This is akin to predicting the rate of global climate variations over millions of years from weather observations collected over just one minute, a rather surprising claim. If the entropy model were correct, how can the liquid configurational entropy possibly be monitored by probing the liquid over just a very brief period of time? This questions and others are also briefly reflected upon in the talk.

References

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[3] J. C. Dyre, Nature Mater. **3**, 749 (2004).