The Two Level Tunneling Systems in Glasses and the Finite Size Effect in Glass Transitions

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Abstract

We discuss a connection between the glass transition and the low temperature properties of glass by examining the elastic dipolar interactions among the two level tunneling systems in glass, suggesting the glass transition to be a spin glass transition–like phase transition among the two level tunneling systems in glass, pointing out that this connection could lead to finite size effect in glass transition, as experimentally observed.

In our recent work [1] we suggested that the glass transition at the transition temperature T_g may well be a spin glass–like phase transition [2, 3, 4, 5, 6, 7] among the two level tunneling systems (TLS) [8, 9] in glass, though we understand that there is no direct experimental evidence that the TLS are relevant to glass transition. In this paper we continue this discussion by examining the finite size effect in glass transition that might result from the inter–TLS interactions as we have proposed. Morineau, Xia, and Alba-Siminesco [10], measuring the heat capacity and thermal expansion of small glass samples, have observed finite size effects in glass transition in liquid toluene porous silicates confined in cylindrical mesopores. They found, among other things, that in pores of radius $\sim 2.4 \ nm$, the glass transition temperature was raised by $37K$, from $117K$ in bulk samples to $154K$ in pores. The finite size effect in spin glass transition has also been observed by Kennig *et al.* [11] The finite size effects in glass dynamics though not in glass transition have also been discussed by Horbach *et al.* [12] and by Riggeleman *et al.*. [13] It is important to note that the glass transition is not an equilibrium thermodynamic phase transition but is fundamentally a kinetic phenomenon, a tremendous slowing down, a huge increase and divergence of the substance's viscosity, [14] all within a narrow interval of temperatures. As such we do not see how any equilibrium thermodynamics treatment, one based on the calculation of the partition function or the application of the results of equilibrium thermodynamics phase transitions, can be relevant. According to one definition, the glass transition temperature T_g is defined as the temperature above which the "molecular structure exhibits macromolecular mobility."[15] One definition for the glass transition temperature provides as the temperature T_g at which the viscosity goes to 10^{12} Pasco-sec, taking into account the dynamic nature of the transition. [14] But it has also been noted that all definitions for the glass transition

temperature are arbitrary, that at best they agree within a few degrees. [14]

A collection of mutually noninteracting particles do not have nonzero finite size effect (indeed would not have phase transition at all). To observe finite size effect, it is essential to take into consideration the inter–particle interactions. At a temperature of $1K$ or below, the phonon wavelength is $\lambda \sim 10^3$ Å or longer, and one really cannot tell much difference between a piece of glass and a piece of crystal. The reason that the low temperature behaviors of glasses are very different from crystals is largely due to the existence of the TLS. The interaction among TLS via exchanges of virtual phonons has been discussed by, among others, Jofferin and Levelut [16] and Black and Halperin [17] for the inter–TLS elastic interaction in glass and their effect on the relaxation rate of dressed TLS. Kassner and Silbey [18] have also considered the inter–TLS interaction and its effect on the relaxation rate of dressed TLS. In bulk glass, the TLS are mutually coupled via long range elastic dipolar interactions. [19] The interaction between two elastic dipoles in bulk medium is: [21]

$$U(r) = \frac{1}{8\pi} \frac{(1+\sigma)(3-4\sigma)}{(1-\sigma)} \frac{\lambda^2}{c_g^2 \rho} \frac{1}{r^3} \equiv \frac{A}{r^3} \tag{1}$$

where, for many glasses, $\sigma \sim 0.2$ is Poisson's ratio, $\lambda \sim 2 \ eV$ is the elastic dipolar moment of one dipole, $c_g \sim 4,000 \ m/s$ is the speed of sound in glass, $\rho \sim 2.5 \ g/cm^3$ is the mass density of the glass, and so we have A $\sim$ 2.1 eV Å^3 . To study the finite size effects of glass behavior and not only its transition, we have suggested to examine the properties of glass fibers inside which the long range elastic dipolar interaction will be screened to become short ranged [19] so that we will have, for two TLS separated by distance z in a fiber of radius a, $U(z) = U_0 \exp(-z/a)$. Following virial theorem [20], the average potential energy U is proportional to the average kinetic energy, which is proportional to T. If we then relate the glass transition temperature T_g to $< U >$ and assume that the two are proportional to each

other, we see then that, comparing the transition temperatures in two fibers of lengths L_1 and L_2 and both of radius a, there is a finite size effect in that their transition temperatures Tg_1 and Tg_2 obey:

$$\frac{Tg_1}{Tg_2} = \frac{(1 - e^{-L_1/a})}{(1 - e^{-L_2/a})} \tag{2}$$

In a first order phase transition, while through nucleation which allows supercooling there may have limited finite size effect arising from the surface tension of the phase boundary, the sign of which depending on the comparative surface free energies of the two phases, a finite size effect is not significant. Thus the glass transition as considered in [22] would not have sizable finite size effects, contrary to what was observed experimentally. [10] It is only in a second order phase transition during which the divergence of the correlation length might be bounded by the finite size of the sample that the transition would have significant finite size effect. Still, we note that the glass transition is neither a first order nor a second order *equilibrium* thermodynamic phase transition but is fundamentally a kinetic transition which does have a finite size effect. As a side remark we note that, for that reason, the spin glass transition, [2] a kinetic transition and has a finite size effect as observed experimentally and studied theoretically, [5] is more appropriately described using time–dependent techniques [4] rather than equilibrium statistical mechanics.

We understand that the finite size effect in glass transition as observed experimentally [10] is in three dimensional samples while here we consider essentially a one dimensional system, making it difficult to compare our result with the experimental findings. We also note that there may well be other sources of finite size effects in glass transitions in addition to what is discussed here. Since the concentration of TLS in glass is around 100 ppm, [8, 9] we estimate the average separation between nearest neighbor TLS to be $\sim 2nm$. Thus in the experiment of [10] the sample size, of radius $\sim 2.5nm$,

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is about the same as the inter–TLS distance. We see therefore that there may not be more than a few TLS in each glass pore in that experiment. Because of that, there is no reason to expect such small "glass" pores to have comparable glass transition (or to have transition at all) temperature as that of the bulk glass if, as we assume, that the TLS are important in affecting the behaviors of glass both at low temperatures and at the transition temperature. That glass transitions have been observed in pores so small may either contradict our suggestion that the TLS are important to glass transition or provide evidence that enough TLS exist in very small glass samples. We compare samples of two different sizes. The bigger pore we assume to be of infinite size. The small one we assume to have the same size as the "tube" radius' a. Therefore the ratio between the two transition temperatures Tg_1 and Tg_2 would be

$$\frac{Tg_1}{Tg_2} = \frac{1 - e^{-(\infty/a)}}{1 - e^{-1}} \approx 1.59 \tag{3}$$

to be compared with the experimental finding of $Tg_1/Tg_2 \approx 1.32$.

References

[1] Y. Fu, "Theory of glass transition and the two level systems in glass", http://www.yaotianfu.org/. (2020).

[2] S. F. Edwards and P. W. Anderson, J. Phys. F **5**, 965 (1975).

[3] D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. **35**, 1792 (1975); Phys. Rev. B **17**, 4384 (1987).

[4] H. Sompolinsky and A. Zippelius, Phys. Rev. Lett. **47**, 359 (1981); Phys. Rev. B **25**, 6860 (1982).

[5] I. A. Fernandez, V. Martin–Mayor, S. Perez–Gaviro, A. Taracon, and A. P. Young, "Phase Transition in Three Dimensional Heisenberg Spin Glass: Finite–Size Scaling Analysis," arxiv:0905.0322.v2. 10 Jul 2009.

[6] G. Parisi, J. Phys. Lett. **41**, L361 (1980).

[7] M. Mézard, G. Parisi, N. Sourlas, G. Toulous, and M. Virasoro, J. de Physique **45**, 843 (1984).

[8] P. W. Anderson, B. I. Halperin, and C. M. Varma, Phil. Mag. **25**, 1 (1972); W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972). For reviews see *Amorphous Solids: Low Temperature Properties*, W. A. Phillips, ed. Springer Verlag, Berlin, 1981; W. A. Phillips, Rep. Prog. Phys. **50**, 1657 (1987).

[9] For an up–to–date discussion and review about the low temperature behaviors of glasses and the two level tunneling systems see C. C. Yu and H. M. Carruzzu, Chap. 5 in *Low–Temperature Thermal and Vibrational Properties of Disordered Solids: A Half–Century of Universal "Anomalies" in Glasses*, M. A. Ramos, ed., World Scientific Press. To appear.

[10] D. Morineau, Y. Xia, and C. Alba-Simionesco, J. Chem. Phys. **117**, 8966 (2002).

[11] G. G. Kennig, D. M. Tennant, C. M. Rost, F. Garrot de Silva, B. J. Walters, Q. Zhai, D. C. Harrison, G. D. Dahlberg, and R. L. Orbach, Phys. Rev. B **98**, 104436 (2018).

[12] J. Horbach, W. Kob, K. Binder, and C. A. Angell, Phys. Rev. E **54**, R5897 (1996).

[13] R. A. Riggeleman, H. N. Lee, M. D. Edger, and J. J. de Pablo, Phys. Rev. Lett. **99**, 215501 (2007).

[14] IUPAC Compedium of Chemical Teminology, 2nd ed. A. D. McNauright and A. Wilkinson, eds. Cambridge, U. K. (1997). One Pascal-sec equals $1\ kg\ m^{-1}\ s^{-1}$.

[15] Rotational Molecule Technology (2020).

[16] J. Joffrin and A. Levelut, J. de Physique **36**, 811 (1973).

[17] J. L. Black and B. I. Halperin, Phys. Rev. B **16**, 2879 (1977).

[18] K. Kassner and R. S. Silbey, J. Phys. Cond. Matt. Phys. **1**, 4599 (1989).

[19] Y. Fu, Phys. Rev. B **40**, 10056 (1989).

[20] L. D. Landau and E. M. Lifshitz, *Mechanics*, 3rd ed., Pergamon Press, Oxford (1976), p. 23.

[21] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, 3rd ed., Pergamon Press, Oxford (1986), p. 26. Numerous typos.

[22] V. Lubchenko and P. G. Wolynes, Ann. Rev. Phys. Chem. **58**, 235 (2007); Adv. Chem. Phys. **136**, 95 (2009).