## Low-Temperature Anomalies in Strong and Fragile Glass Formers

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The low-temperature anomalies of glass forming systems are analyzed focusing on the concept of fragility. It is shown that two extremes on the fragility plot,  $SiO_2$  and  $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ , show a strong difference in specific heat in the range of excess vibrational contribution. This difference cannot be explained in the framework of the soft potential model in its present state. A relation between the excess vibrational contribution and the amount of structural fluctuations is suggested. It is shown that the suggested relation explains the found difference in low-temperature specific heat between strong and fragile glass formers. [S0031-9007(97)02799-3]

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Low-temperature anomalies, which were found to be universal for different kinds of glasses [1], are still a puzzle in the physics of condensed matter. First, they show up at very low temperatures (T < 1 K) as an anharmonic contribution, producing a linear term in specific heat  $C_p$ . Then, at higher temperatures ( $T \sim$ 5-10 K), the so-called excess vibrational contribution appears as a bump in  $C_p/T^3$ . However, it is still not clear whether these two anomalies (anharmonic and harmonic ones) are related to each other or are two independent contributions, and how they are related to structural disorder.

The anharmonic contribution at lowest T was successfully described in the framework of the two-level-systems (TLS) approach [1], although the microscopic nature of TLS and their universality are still not clear. Later this approach was extended to the soft potential model (SPM), which includes also the above-mentioned excess vibrational contribution [2,3]. SPM assumes that both the TLS and the excess vibrations appear from soft anharmonic potentials, and it predicts a strong relation between these two contributions.

New interest in this problem was stimulated by recent suggestions about the relation of the low-temperature anomalies with glass transition dynamics [4–7]. In particular, it was noted that the ratio between TLS and the excess vibrational contributions correlates with the degree of fragility of the system [6]. Fragility is a property of glass forming liquids at temperature above the glass transition  $T_g$  [8], and thus some correlation between the low-temperature anomalies and the properties of the supercooled melt was suggested [6].

The aim of this Letter is a comparison of the lowtemperature specific heat in two glasses which are extremes on the fragility scale [SiO<sub>2</sub>, which is the strongest, and  $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$  (CKN), which is one of the most fragile systems], in order to test the suggested relation between the low-temperature anomalies and the degree of fragility, and to test also whether the SPM predictions can describe the properties of fragile systems.

The CKN sample was prepared in the way described in [9]. The sample was annealed during ~100 hours at T = 320-325 K. The specific heat of CKN was measured in the way described previously in [10] and is shown in Fig. 1. At T < 1 K it is in a reasonable agreement with the data from Stephens [11]. Estimation of the linear term in the specific heat gives  $C_1 \approx 51 \text{ erg/g K}^2$ , also in reasonable agreement with the known data [11]. An important result is that the bump in  $C_p/T^3$  at  $T \approx 6$  K is hardly pronounced in the case of CKN (Fig. 1). This result seems to be general for fragile systems; in particular, for another extremely fragile glass former polyvinyl chloride (PVC) the bump is even less pronounced (see inset of Fig. 1) [10].

Figure 2 shows comparison of  $SiO_2$  and CKN specific heat data. Also the data for Se, which is some intermediate case on the fragility scale, are shown. It is not clear how to do properly a quantitative comparison of the data for systems with different chemical composition. One of the ways is the scaling of all parameters with the values expected in the Debye model. If the substances would differ only by density and elastic constant (sound velocities), then after scaling with the Debye values (*we would like to stress that both axes are scaled*) they should



FIG. 1. The specific heat of CKN: ( $\bigcirc$ ) these measurements, ( $\triangle$ ) data from [11]. Dashed line shows the expected Debye level ~79 erg/gK<sup>4</sup> [11], and the solid line shows a sum of the Debye and TLS contribution with  $C_1 = 51 \text{ erg/g K}$ . The inset shows the specific heat of another extremely fragile glass former PVC; data from [10].

show a similar behavior. Surprisingly the TLS contribution in this presentation is rather similar in these glasses (a bit higher in CKN), while the excess vibrational contribution differs significantly. Figure 3 presents the ratio of the excess vibrational contribution to the Debye value  $C_{\text{exc}}/C_D = (C_p/C_D - 1)$  vs degree of fragility *F* for a few glass formers. It reveals a strong correlation between this ratio and the degree of fragility. A similar analysis of the linear term in the specific heat does not show any clear tendency but rather a scattering of the points (see, for example, a table in [11]); i.e., there is no direct or strong correlation between TLS contribution and the degree of fragility. The absence of the direct correlation was also deduced in [10] from the experiments on PVC, where de-



FIG. 2. The specific heat scaled by the Debye value  $C_D$  vs temperature scaled by the Debye temperature  $T_D$  for SiO<sub>2</sub> Heralux (from [12]) (solid line) and Suprasil I (from [13]) (•), Se (from [14]) (•), and CKN ( $\triangle$ ). The Debye parameters are taken from [11]. The inset shows the excess specific heat scaled at the linear term and plotted vs  $T/T_{\min}$ ,  $T_{\min} = 2.3$  K for Heralux, =2 K for Suprasil I and =2.15 K for CKN. The dashed lines show extrapolation of the temperature dependence of  $C_{\text{exc}}/T^3$ .

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pendence of TLS concentration on the sample preparation was found.

Let us now consider briefly the main predictions of SPM. The basic SPM assumption is the existence of three kinds of excitations in the frequency (or temperature) range of interest: (i) sound waves (Debye contribution), (ii) TLS with specific heat

$$C_{p\text{-}TLS} \approx 0.61 \pi^2 P_0 \eta^{2.5} k^2 T W^{-1} \\ \times \{ \ln[(t_{\exp}/\tau_{\min})^{0.5} W/kT] \}^{1/3} \approx C_1 T, \quad (1)$$

and (iii) quasiharmonic soft oscillators (HO) with the specific heat directly related to that of TLS

$$C_{p-\text{HO}} \approx 0.09 \pi^6 k P_0 \eta^{2.5} (kT/W)^5 \approx b C_1 T (kT/W)^4.$$
(2)

Here *b* is a constant  $b \approx 7-8$ , *W* is a characteristic energy of the model  $W \approx (2-2.5)kT_{\text{min}}$ , where  $T_{\text{min}}$  is the temperature of the minimum in  $C_p/T^3$ ; for the other parameters see [2,3]. Essential prediction of SPM in its present state [3] is an increase of the density of HO states with energy in fourth power  $g_{\text{HO}} \propto \omega^4$  and, as a consequence,  $C_{p-\text{HO}} \propto T^5$ . It is based on the assumption that the fourth order term in displacement is the leading term, which stabilizes the soft potential. From comparison with experimental results it was shown that these SPM predictions describe well various data for SiO<sub>2</sub> [2,3], phosphate, and some other rather strong glass formers [15].

The question arises, however, whether these SPM predictions are valid for glasses in general and, in particular, for extremely fragile ones. According to SPM [Eqs. (1) and (2)] the excess  $C_p$  scaled at the linear term [Eq. (1)] and plotted vs temperature scaled by  $T_{min}$  should have universal behavior around  $T_{min}$  for different glasses. However, even in this presentation (inset of Fig. 2) a strong difference appears between SiO<sub>2</sub> and CKN. The results in Fig. 2 show that there is no direct relation between density of TLS and of the excess vibrations.



FIG. 3. The ratio of the excess specific heat to the Debye value around the maximum (at  $T \sim 3-10$  K) vs degree of fragility *F* (for definition, see [6]). All data are from [6] and references therein, except for CKN data, which are from the present work.

This conclusion can also be supported from an analysis of literature data. For example, doping of silica glass by sodium oxide with concentration more than 20% increases the linear term in  $C_p$  [11,16], whereas the excess vibrational contribution decreases significantly [16]; if a restricted temperature interval (T > 0.4 K) used in [17] can be considered as appropriate for estimation of the linear term in  $C_p$ , quenching of B<sub>2</sub>O<sub>3</sub> glass appears to increase the linear term in  $C_p$  more than 6 times, whereas the excess vibrational contribution increases much weaker (less than 2 times) [17]. Another prediction of SPM [3], the asymptotic behavior  $C_{p-HO} \propto T^5$  [Eq. (2)] which has been found earlier in rather strong glass formers [3,15], also does not show up in CKN (inset of Fig. 2). Unfortunately, the Debye parameters are not known for PVC. But even without detailed analysis one can see the same deviations from this asymptotic SPM prediction for this very fragile system: At  $T > T_{\min}$  the specific heat increases rather like  $C_p \sim T^3$  (see inset of Fig. 1).

There is another approach for explanation of the excess vibrational density of states [18–21]: Many authors relate it to strong scattering of vibrations caused by fluctuations of elastic constants and/or density in disordered structures. The scattering leads to a drastic decrease of the mean free path of vibrations  $L(\omega)$  and, in particular, can increase the vibrational  $g(\omega)$  in a certain frequency range [21,22]. Here we propose a simple way to consider how a decrease of  $L(\omega)$  can produce an increase in the vibrational  $g(\omega)$ .

In a general case the vibrational density of states can be written in terms of propagator or elastic response function  $D(k, \omega)$  (see, for example, [21–24]),

$$g(\omega) \propto -\omega \operatorname{Im}\left\{\int_{0}^{k_{D}} d^{3}k D(k,\omega)\right\},$$
 (3)

where  $k_D$  is a Debye cutoff. The elastic response function for acoustic vibrations in the hydrodynamic limit can be written as [24,25]

Im{
$$D(k, \omega)$$
}  $\propto -\omega F''(k) / \{ [\omega^2 - v_{\infty}^2 k^2 + \omega F'(k)]^2 + [\omega F''(k)]^2 \}.$  (4)

Here  $v_{\infty}$  is the sound velocity at high frequency, F(k) is a function, which characterizes damping of the vibration. In particular, the lifetime of the vibration is  $\tau \approx 2/F''(k)$ . In an ideal crystal at low temperatures  $F(k) \rightarrow 0$ , Im{ $\omega D(k, \omega)$ } is essentially the delta function  $\delta(\omega^2 - k^2 v_{\infty}^2)$ , and one gets from Eq. (3) the usual Debye density of states  $g(\omega) \propto \omega^2$ . However, the finite value of F(k) changes  $g(\omega)$ : The damping [Eq. (4)] gives broadening and shift to lower  $\omega$  for the vibrational response and also some additional response at low frequencies.

Often the damping due to elastic scattering on structural fluctuations is neglected and only the damping due to some relaxation processes is analyzed. We suggest to analyze the inverse situation: Let us consider the damping due to "frozen in" fluctuations and neglect the damping due to relaxation processes. The main problem here is to find the damping function F(k). One can relate it to the mean

free path of the vibration:  $F''(k) \approx 2/\tau \approx 2v_{\infty}/L(k)$ . It is well known from analysis of thermal conductivity data that in the frequency range around the boson peak L(k)decreases  $\propto k^{-4}$ , reaches the Ioffe-Regel criterion  $kL(k) \sim$ 1, and is nearly constant at large  $\omega$  [26,27]. So, one can write  $L(k) \approx 1/Gk^4 + L_0$ , where  $L_0$  is a minimum value (in different approaches it is either  $L_0 \approx \text{const} \sim$  $1/k_D$  or  $L_0 \sim 1/k$  [26,27]) and *G* describes the scattering. In particular, *G* can be derived from the amplitude of fluctuations of average sound velocity  $\langle \Delta v^2 \rangle$  together with the spatial correlation length of the fluctuations  $R_c$  [26]:  $G = 8R_c^3 \langle (\Delta v/v)^2 \rangle$ . Thus we assume for F''(k)

$$F''(k) = 2\nu_{\infty}/(1/Gk^4 + L_0).$$
 (5)

The behavior of F'(k) is not clear, and we analyzed two cases: (i) F'(k) = F''(k), because it is known that  $F'(k) \approx$ F''(k) for the case of maximum damping due to relaxation processes; and (ii) F'(k) = 0. Figure 4 shows results of numerical calculations of Eq. (3)–(5), using  $\omega = v_{\infty}k$ , for three sets of parameters G and  $L_0$ . One can see that an increase of G leads to a strong increase of  $g(\omega)$  in the lowfrequency range. This qualitative result is independent of our choice of F'(k) and shows that decrease of the mean free path of the vibrations shifts the states to lower frequency (Fig. 4). The choice of  $L_0$  (~const, or ~1/k) also does not change the qualitative result; it is important that  $\omega F''(k)$  first increases with k and then at some certain  $\omega$  decreases or is ~const. We would like to note that the suggested consideration is similar with the approach used for description of the phonon-fracton crossover [22], which was found to be in a good agreement with the light scattering experiments on silica aerogels [28].

Thus the simple qualitative arguments suggest an explanation for the difference in the density of vibrational states between strong and fragile glass formers (Figs. 2 and 3): The amount of structural fluctuations, G, is larger



FIG. 4. Estimation of  $g(\omega)/\omega^2$  assuming F'(k) = F''(k)(solid lines) and F'(k) = 0 (dashed lines) and parameters  $L_0 = 1$ ,  $G = 10^{-4}$  (1), G = 1 (2), and G = 10 (3); all parameters are given in units of  $k_D$ .

in strong systems and smaller in fragile ones. This suggestion seems to be reasonable, if one compares the microstructures of SiO<sub>2</sub> and CKN: Strong fluctuations are expected in a rigid 4-coordinated structure of SiO<sub>2</sub>, and rather weak ones should show up in CKN, where movable ions will smooth any fluctuations. However, this suggestion has also some consequences. It is known that the quenching of the glass forming system will change the amplitude of the fluctuations: the higher the cooling rate the larger will be the amplitude. So, one would expect an increase of the excess  $g(\omega)$  in quenched samples. Analysis of the literature data [17,29,30], indeed, supports this suggestion. Another prediction can be done for low-temperature thermal conductivity, where so-called "plateau" between 1 and 10 K is usually ascribed to the regime  $L(k) \propto k^{-4}$  [26,27]: Weaker scattering of the vibrations in more fragile systems should give less pronounced "plateau" in thermal conductivity. Analysis of literature data shows that the predicted difference in the thermal conductivity appears at least as a tendency inside one type of glass formers; for example, the plateau is well pronounced in polymethyl methacrylate (PMMA) [26] and has nearly vanished in more fragile polymer PVC [10]; doping of B<sub>2</sub>O<sub>3</sub> glass by Na<sub>2</sub>O makes it more fragile [31], and the plateau in thermal conductivity becomes less pronounced [32]; the plateau is nearly vanished in the case of extremely fragile CKN [33]. So, the detailed analysis of the thermal conductivity of glass forming systems from the point of view of their fragility can shed new light on the origin of the plateau.

Thus, the results presented above show that there is strong correlation between one part of the low-temperature anomalies and the degree of fragility of glass forming systems. The comparison of glasses which differ strongly in the fragility plot shows explicitly that there is no direct relation between the density of TLS and of the excess vibrational contribution. This conclusion is in contradiction with a basic prediction of SPM, and it appears that the model has to be revised at that point. It is shown that spatial damping due to fluctuations in disordered structure may be a reason for the excess vibrational excitations. The difference between strong and fragile systems can be related in this case to the difference in the amount of fluctuations (parameter G): It is large for strong systems and small for fragile ones. The correlation between the excess vibrational contribution and the degree of fragility supports the idea that the former influences strongly the dynamics of the glass transition.

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- [1] Amorphous Solids: Low-Temperature Properties, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981).
- [2] V. G. Karpov, M. I. Klinger, and F. N. Ignatiev, Sov. Phys. JETP 57, 439 (1983).
- [3] U. Buchenau, Yu. M. Galperin, V. L. Gurevich, and H. R. Schober, Phys. Rev. B 43, 5039 (1991).
- [4] U. Buchenau and R. Zorn, Europhys. Lett. 18, 523 (1992).
- [5] V. K. Malinovsky and V. N. Novikov, J. Phys. Condens. Matter 4, L139 (1992).
- [6] A. P. Sokolov, E. Rössler, A. Kisliuk, and D. Quitmann, Phys. Rev. Lett. 71, 2062 (1993).
- [7] L. Gil, M. A. Ramos, A. Bringer, and U. Buchenau, Phys. Rev. Lett. 70, 182 (1993).
- [8] C. A. Angell, in *Relaxation in Complex Systems*, edited by K. L. Ngai and G. B. Wright (Office Naval Res., Washington, 1984), p. 3.
- [9] E. Rössler et al., Phys. Rev. B 49, 14967 (1994).
- [10] E. Duval et al., J. Non-Cryst. Solids 190, 258 (1995).
- [11] R.B. Stephens, Phys. Rev. B 8, 2896 (1973); Phys. Rev. B 13, 852 (1976).
- [12] U. Buchenau et al., Phys. Rev. B 34, 5665 (1986).
- [13] H. v. Löhneysen, H. Rüsing, and W. Sander, Z. Phys. B 60, 323 (1985).
- [14] J. C. Lasjaunias and R. Maynard, J. Non-Cryst. Solids 6, 101 (1971).
- [15] A. Brodin *et al.*, Phys. Rev. Lett. **73**, 2067 (1994);
   G. Carini *et al.*, Phys. Rev. B **52**, 9342 (1995).
- [16] G. K. White, J. A. Birch, and M. H. Manghnani, J. Non-Cryst. Solids 23, 99 (1977).
- [17] M. A. Ramos et al., in Proceedings of the Second International Workshop on Non-Crystalline Solids, edited by J. Colmenero and A. Alegria (World Scientific, Singapore, 1990), p. 514.
- [18] A. P. Sokolov, A. Kisliuk, M. Soltwisch, and D. Quitmann, Phys. Rev. Lett. 69, 1540 (1992).
- [19] E. Duval, A. Boukenter, and T. Achibat, J. Phys. Condens. Matter 2, 10 227 (1990).
- [20] S.R. Elliott, Europhys. Lett. 19, 201 (1992).
- [21] W. Schirmacher and M. Wagener, Solid State Commun. 86, 597 (1993).
- [22] G. Polatsek et al., Phys. Rev. B 39, 9353 (1989).
- [23] P. Fulde and H. Wagner, Phys. Rev. Lett. 27, 1280 (1971).
- [24] G. Winterling, Phys. Rev. B 12, 2432 (1975).
- [25] J.P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
- [26] J. E. Graebner, B. Golding, and L. C. Allen, Phys. Rev. B 34, 5696 (1986), and references therein.
- [27] P.B. Allen and J.L. Feldman, Phys. Rev. B 48, 12581 (1993).
- [28] E. Courtens et al., Europhys. Lett. 6, 245 (1988).
- [29] N. Ahmad, K. W. Hutt, and W. A. Phillips, J. Phys. C 19, 3765 (1986).
- [30] S.L. Isakov et al., Solid State Commun. 86, 123 (1993).
- [31] G. D. Chryssikos *et al.*, J. Non-Cryst. Solids **172–174**, 378 (1994).
- [32] R. Villar, M.A. Lopez de la Torre, and S. Vieira, Phys. Rev. B 34, 7394 (1986).
- [33] D.G. Cahill and R.O. Pohl, Phys. Rev. B 35, 4067 (1987).