

# PHYSICAL REVIEW B

## CONDENSED MATTER AND MATERIALS PHYSICS

THIRD SERIES, VOLUME 61, NUMBER 14

1 APRIL 2000-II

### RAPID COMMUNICATIONS

*Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in Physical Review B may be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

#### Contribution of floppy modes to the heat capacity jump and fragility in chalcogenide glasses

Gerardo G. Naumis

*Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Apartado Postal 20-364, 01000 Distrito Federal, Mexico*

(Received 21 September 1999)

The jump of the heat capacity in chalcogenide glasses during glass transition is estimated using the number of floppy modes as a free energy. A comparison with experimental data shows good agreement, without using any free parameter. This result allows a determination of the change of the glass fragility and excess thermal expansivity as a function of the average coordination number.

Glass transition is one of the most fascinating problems in physics, but also it remains as one of the most challenging ones. Although this transition has considerable practical and technological importance, still there is no consensus about which thermodynamical and structural factors determine the glass transition temperature ( $T_g$ ).<sup>1</sup> For chalcogenide glasses, attention has been devoted to correlate  $T_g$  with other physical and chemical properties,<sup>2</sup> since such glasses have electric and infrared transmission properties that make them useful in technological applications.<sup>3</sup> One of these interesting problems is the change in the properties of the glass as the chemical composition is changed. For example,  $T_g$  and  $\Delta C_p$  (the jump in the specific heat in the glass transition) can be raised or lowered by adding impurities, and the fragility of the glass can be changed from fragile to strong.<sup>4</sup> For the first case, a method based on the statistics of agglomeration processes<sup>5-9</sup> has succeeded in obtaining the empirical modified Gibbs-DiMarzio law, that allows a calculation of the change of  $T_g$  as a function of the concentration of modifiers.<sup>3</sup> Furthermore, the method predicts the correct value of the constant that appears in the Gibbs-DiMarzio law for almost any chalcogenide glass,<sup>9</sup> and shows its topological origin.<sup>5</sup> The changes of  $\Delta C_p$  and fragility as a function of the composition has been less studied, but there is some experimental work on the subject.<sup>10,4,11,12</sup>

Of fundamental importance to all of these problems is the constraint theory introduced by Phillips<sup>13</sup> and further refined by Thorpe.<sup>14,15</sup> Phillips considered the mechanical constraints experienced by an atom in order to explain the ability for making glass. Constraints produce floppy modes in the network, which have zero frequency. By considering a Kirkwood-Keating type of potential, it can be shown<sup>13</sup> that

the fraction of floppy modes available in a network is  $f = 2 - (5\langle r \rangle / 6)$ , where  $\langle r \rangle$  is the average coordination number. Of special importance is the point  $\langle r \rangle = 2.4$ , where the number of floppy modes is zero. This point was recognized by Thorpe to be a “rigidity transition,”<sup>14</sup> between a floppy network and a rigid one; it corresponds to a strong tendency for making glass. Although the introduction of the floppy modes and the average coordination number has stimulated much work to test this theory, not so much effort has been done in order to test the theory in a quantitative way.

In this paper, I report the use of the floppy mode theory in order to obtain the jump in the specific heat of the glass as a function of  $\langle r \rangle$ . To do this, we will consider the number of floppy modes as a free energy. The idea is to connect the entropy of the liquid phase, with the range of possible disordered structures, since rigidity percolation operates more effectively in the liquid state of the chalcogenide systems.<sup>10</sup> As we will also see, this idea also allows an explanation of the change in fragility of the glass—which in some sense gives an idea of the “difficulty degree” for making the glass—and the functional form of the excess expansion coefficient.

We start by making the observation that below  $T_g$ , the specific heat of the glass must be  $3Nk \approx 6$  (cal/mol K), independent of  $\langle r \rangle$ , if the constraints do not affect the total number of degrees of freedom for harmonic vibrations. This comes from the equipartition of energy, since the kinetic and vibration energy contributes each with  $NkT/2$ , as in the Dulong-Petit law. The experimental data by Senapati and Varshneya<sup>10</sup> show that  $C_p$  is nearly 6 cal/(mol K) for all  $\langle r \rangle$  in the glassy state. Thus, in this case the floppy modes do not affect the internal energy. The observance of the Dulong-Petit law for the glass also means that the problem can be

treated as classical, and that floppy modes do not have a perfect zero frequency, because in such a case, from statistical mechanics, we can expect a reduction of the internal energy proportional to the number of constraints.

In the liquid melt, there is more room for the system to explore the energy landscape. This fact suggests that floppy modes can be more important since they produce regions of less rigidity, and thus these regions are more suitable to produce a richer landscape. The idea is to relate floppy modes with the presence of local regions with less stress in the system, i.e., we relate low-frequency vibrational modes with disorder, since configurational modes have been shown to explain the additional specific heat of the melt,<sup>16</sup> and these configurational modes are identified with the degree of stress. Observe that in principle, floppy modes are eigenvectors of the dynamical matrix with zero frequency in the glass, but in the supercooled and normal liquid phase, this matrix is not well defined, except if we consider that the eigenmodes can be identified with *instantaneous normal modes*.<sup>16</sup> However, rigidity is a static concept, involving virtual displacements, so while it is useful to use a dynamical matrix for a given potential, any set of pair potentials would give the same results for geometric aspects of rigidity,<sup>17</sup> which are the ones that concern us in the present work.

In order to test these ideas, we start by evaluating the internal energy of the liquid melt as a sum of various terms:

$$U = U_{kin} + U_{harm} + U_{anharm} + U_{flo}, \quad (1)$$

where  $U_{kin}$  is the contribution from the kinetic energy of the atoms,  $U_{harm}$  comes from the harmonic vibrations, and  $U_{anharm}$  is the contribution from anharmonic terms of the interatomic potential. Finally,  $U_{flo}$  is the contribution that we will assume depends on the number of floppy modes. The fact that we separate anharmonic and floppy modes deserves some words. As was said previously, the shape of the pair potential does not affect the existence of floppy modes, it only changes the small finite frequency of these modes. In fact, these modes we expect to be more related with terms in the potential that produce stress, as for example what happens in the modified soft model, where a linear term is added in order to account for stress.<sup>16</sup> As we will see, anharmonic terms are related to melting, while we suppose that floppy modes are related to configurational modes and relaxation of strain.

Now we can use the equipartition theorem which gives the contribution of the kinetic energy,  $U_{kin} = 3NkT/2$ . For the harmonic contribution, we must remember that liquids cannot withstand shear stress, and thus they cannot sustain transverse modes of vibration, therefore, they have only  $N$  vibrational modes, corresponding to longitudinal phonons. The contribution from this term is  $U_{harm} = NkT/2$ . The third and fourth term are responsible for nucleation and crystallization. However, when we are at the rigidity threshold ( $\langle r \rangle = 2.4$ ), we expect the last term to vanish since there are not floppy modes available. In such a case,  $U_{anharm}$  can be calculated using an argument put forward by Phillips.<sup>13</sup> He supposed that this term must be roughly equal to the first near the glass transition, i.e.,  $U_{anharm} \approx 3NkT/2$ , since the first term corresponds to the activation energy barrier for local melting and the anharmonic term is the thermal driving force of unrelaxed configurational energy.<sup>13</sup>

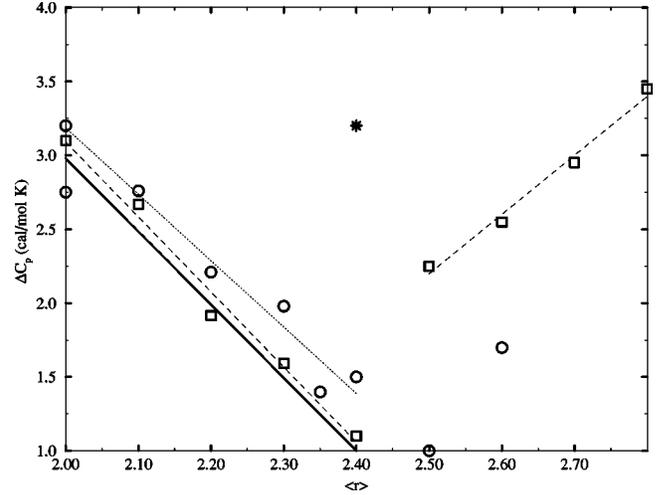


FIG. 1.  $\Delta C_p$  as a function of  $\langle r \rangle$ . The line corresponds to Eq. (3). Experimental data from Ref. 4 are shown with squares. The star corresponds to  $As_2Se_3$ . A best fit line is shown with a dashed line. The circles correspond to the data of  $Ge_xSe_{1-x}$  from the work of Feng *et al.*<sup>11</sup> The dotted line corresponds to the best fit of their data. Other symbols correspond to the data of Chang and Bestul<sup>19</sup> (diamond) and Moynihan *et al.*<sup>20</sup> (star).

Finally, we will assume that  $U_{flo}$  is a function of the number of floppy modes. We suppose that each mode acts as an effective extra degree of freedom for relaxation in the region where  $\langle r \rangle < 2.4$ . According to the equipartition theorem, each mode contributes with  $kT/2$  to  $U$ . Thus,  $U_{flo}$  is proportional to  $f3NkT$ . This idea is consistent with the work of Duxbury *et al.*, who showed that the number of floppy modes behaves as a free energy for both connectivity and rigidity percolation.<sup>18</sup> In fact, a specific heat can be defined using the second derivative of the free energy.<sup>18</sup> By adding these contributions, we find the specific heat to be,

$$C_p(\text{melt}) = \frac{7Nk}{2} + 3Nk \left( 2 - \frac{5\langle r \rangle}{6} \right), \quad (2)$$

from where the jump in the specific heat between the glass and the melt ( $\Delta C_p$ ) is given by

$$\Delta C_p = C_p(\text{melt}) - 3NkT = Nk \left( 13 - \frac{5\langle r \rangle}{2} \right). \quad (3)$$

In Fig. 1 we plot Eq. (3), and  $\Delta C_p$  from the experimental data of  $As_xGe_ySe_{1-x-y}$  and  $Ge_xSe_{1-x}$ ; taken from the work of Tatsumisago *et al.*<sup>4</sup> (squares), Feng *et al.*<sup>11</sup> (circles), Chang and Bestul<sup>19</sup> (diamond) and Moynihan *et al.*<sup>20</sup>  $As_xGe_ySe_{1-x-y}$  and  $Ge_xSe_{1-x}$  systems are used because they are a benchmark test for the constraint theory; especially the first system since a given average coordination number can be reached with many different compounds. For this reason, in the  $As_xGe_ySe_{1-x-y}$  system, each set of data corresponds to several chemical compositions which give the same  $\langle r \rangle$ . From the figure, we observe that although Eq. (3) does not have free parameters, it gives a good fit of the experimental data. One special exception is the binary  $As_2Se_3$  (shown as a star), which is atypical in the sense that it does not follow the isocoordination rule in its properties. Probably, this is related to its ‘raft’-like structures of two

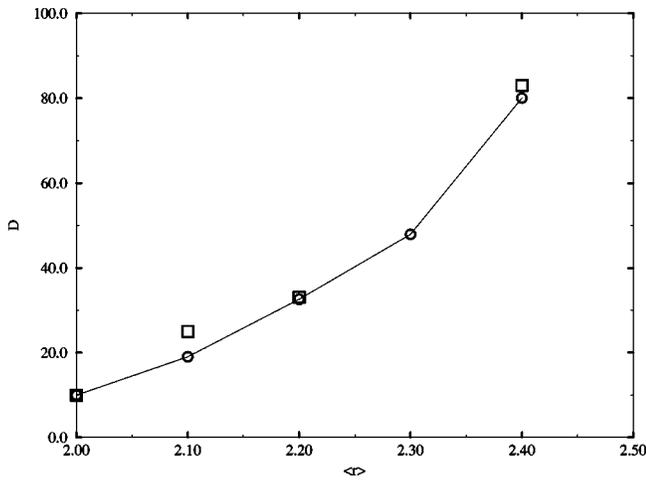


FIG. 2.  $D$  as a function of  $\langle r \rangle$ . The squares are from Ref. 4. The circles are the values obtained from Eq. (8), and the line is a visual guide.

dimensional aspect.<sup>4</sup> If we exclude this point, then a linear regression of the experimental data from the work of Tatsumisago *et al.* gives a slope of  $-5.07$  cal/(mol K), with a correlation of 0.993, which is very similar to the value of  $-4.96$  cal/(mol K) predicted by the floppy mode approach. This best fit is shown as a dashed line in Fig. 1. The data from the work of Feng *et al.*, give a slope for the best fit of  $-4.76$ , with a correlation of 0.985 (shown as a dotted line). For the overconstrained region ( $\langle r \rangle > 2.4$ ), there is a work by Phillips which gives the form of the internal energy,<sup>13</sup> but we can observe that in this regimen  $\Delta C_p$  is also linear with a slope of 4 cal/(mol K) and correlation 0.991.

The magnitude of the jump in  $C_p$  at the glass transition is also related with the fragility of the glass. Strong glass forming liquids are resistant to changes in the medium range order<sup>1</sup> because the amount of configurational entropy in the liquid is relatively small. Fragile glass forming liquids have a high entropy. The relation of this configurational entropy ( $S_c$ ) with  $\Delta C_p$  comes from the expression,<sup>21</sup>

$$S_c = \int_{T_k}^T \Delta C_p d(\ln T), \quad (4)$$

where  $T_k$  is the Kauzmann liquid-crystal isoentropy temperature. In the present approach, from Eq. (3) it is clear that  $S_c$  has a linear dependence on  $\langle r \rangle$ , i.e., fragility is related with the number of floppy modes. A key quantity that allows to classify the fragility of the glass is the behavior of the viscosity. Fragile glasses forming liquids follow the Volger-Fulcher law,<sup>1</sup>

$$\eta = \eta_0 \exp(DT_0/(T - T_0)), \quad (5)$$

where  $D$  and  $T_0$  are constants. Strong glasses follow an Arrhenius law. However, both behaviors are to be expected from the Adam-Gibbs equation,<sup>22</sup>

$$\eta = \eta_0 \exp(C/TS_c) \quad (6)$$

since if  $\Delta C_p$  is small, from Eq. (4),  $S_c$  is almost  $T$  independent and Eq. (6) follows an Arrhenius form. The Vogel-Fulcher law is recovered from Eq. (6) when  $\Delta C_p$  is bigger,

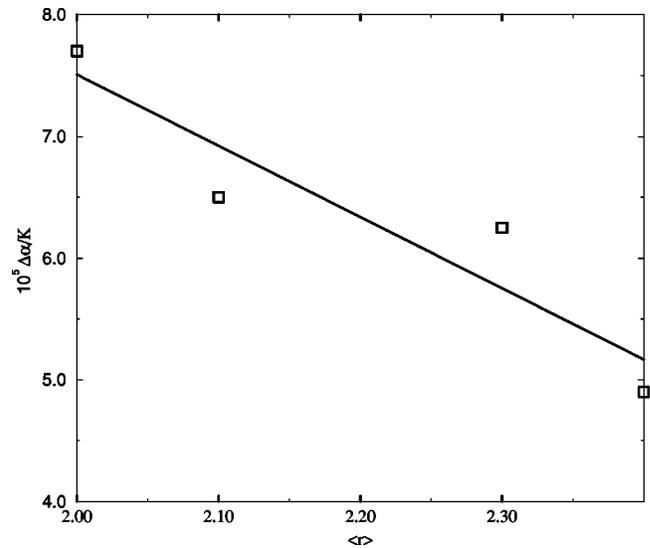


FIG. 3.  $\Delta \alpha$  as a function of  $\langle r \rangle$ . The line corresponds to the best fit.

with a functional form of the type  $B/T$ ,<sup>23</sup> where  $B$  is a constant that must be adjusted in order to account for the total value of  $\Delta C_p$ :

$$B = \Delta C_p \frac{T_K T_m}{T_m - T_K} = Nk \left( 13 - \frac{5\langle r \rangle}{2} \right) \frac{T_K T_m}{T_m - T_K} \quad (7)$$

and  $T_m$  is the temperature where  $C_p$  begins to descend. Using this expression and Eq. (6), the constant  $D$  of the Volger-Fulcher law is given by

$$D = C \frac{T_m - T_K}{NkT_K T_m \left( 13 - \frac{5\langle r \rangle}{2} \right)}, \quad (8)$$

which is a measure of the strength of the liquid. Higher values of  $D$  correspond to strong glasses. The relation defined by Eq. (8) between  $D$  and  $\langle r \rangle$  can be tested with the experimental data, if the constant  $C$  is fixed from one of the experimental points. For pure Se, the experimental data<sup>4</sup> shows that  $D = 10$ ,  $T_K = 240$  K and  $T_m \approx 1.05T_g = 320$  K, to give  $C = 38400$  cal/mol. Using this constant and the values of  $T_K$  and  $T_m$  from the experiment,<sup>10,4</sup> from Eq. (8) we obtain the points that are shown with circles in Fig. 2. The experimental data of Tatsumisago *et al.*<sup>4</sup> are shown with squares in Fig. 2. As it can be seen, there is a good correspondence between the prediction of Eq. (8) and the experimental data.

Another quantity of interest is the excess expansion coefficient ( $\Delta \alpha$ ). The present approach allows to obtain its functional form, although we cannot obtain the values of the constants. According to the free volume theory, we expect that  $\Delta \alpha / \Delta C_p \approx \text{const}$ , thus  $\Delta \alpha$  is of the form:

$$\Delta \alpha \approx C_1 - C_2 \langle r \rangle, \quad (9)$$

where  $C_1$  and  $C_2$  are two constants. This can be corroborated in Fig. 3, where we show a plot of the experimental data for  $\Delta \alpha$  in the  $\text{As}_x\text{Ge}_y\text{Se}_{1-x-y}$  system<sup>4</sup> and the corresponding

linear regression, which has the following form:  $10^5 \Delta \alpha / K = 19.05 - 5.83 \langle r \rangle$ , with a correlation coefficient of 0.936.

We have used the number of floppy modes as a free energy in order to obtain the jump in the specific heat. This approach reproduces the experimental slope of  $\Delta C_p$  versus  $\langle r \rangle$ , without any free parameter. Using this result, the

changes in fragility and expansion coefficients as a function of the average coordination number are obtained.

I would like to thank R. Kerner, R. Barrio, and M. Micoulaut for enlightening discussions, DGAPA-UNAM Project Nos. IN-119698 and IN-108199, and CONACyT Grant No. 25237-E for financial help.

- 
- <sup>1</sup>S.R. Elliot, *Physics of Amorphous Materials* (Wiley, New York, 1989).
- <sup>2</sup>L. Tichý, H. Tichá, *Mater. Lett.* **21**, 313 (1994).
- <sup>3</sup>A.N. Sreeram, D.R. Swiler, and A.K. Varshneya, *J. Non-Cryst. Solids* **127**, 287 (1991).
- <sup>4</sup>M. Tatsumisago, B.L. Halfpap, J.L. Green, S.M. Lindsay, and C.A. Angell, *Phys. Rev. Lett.* **64**, 1549 (1990).
- <sup>5</sup>R. Kerner, *Physica B* **215**, 267 (1995).
- <sup>6</sup>G.G. Naumis and R. Kerner, *J. Non-Cryst. Solids* **231**, 111 (1998).
- <sup>7</sup>G.G. Naumis, *J. Non-Cryst. Solids* **232–234**, 600 (1998).
- <sup>8</sup>M. Micoulaut, *Eur. J. Phys.* **1B**, 277 (1998).
- <sup>9</sup>M. Micoulaut and G.G. Naumis, *Europhys. Lett.* **47**, 568 (1999).
- <sup>10</sup>U. Senapati and A.K. Varshneya, *J. Non-Cryst. Solids* **185**, 289 (1995).
- <sup>11</sup>X. Feng, W.J. Bresser, and P. Boolchand, *Phys. Rev. Lett.* **78**, 4422 (1997).
- <sup>12</sup>W. Bresser, P. Boolchand, and P. Suranyi, *Phys. Rev. Lett.* **56**, 2493 (1986).
- <sup>13</sup>J.C. Phillips, *J. Non-Cryst. Solids* **34**, 153 (1979).
- <sup>14</sup>M.F. Thorpe, *J. Non-Cryst. Solids* **57**, 355 (1983).
- <sup>15</sup>H. He and M.F. Thorpe, *Phys. Rev. Lett.* **54**, 2107 (1985).
- <sup>16</sup>U. Zürcher and T. Keyes, in *Supercooled Liquids*, edited by J.T. Tourkas, D. Kivelson, U. Mohanty, and K.A. Nelson (American Chemical Society, Washington, D.C., 1997) pp. 82–94.
- <sup>17</sup>M.F. Thorpe, D.J. Jacobs, N.V. Chubinsky, and A.J. Rader, in *Proceedings of the Conference Rigidity Theory and Applications, Traverse City, Michigan, 1998* (Plenum, New York, in press).
- <sup>18</sup>P.M. Duxbury, D.J. Jacobs, M.F. Thorpe, and C. Moukarzel, *Phys. Rev. E* **59**, 2084 (1999).
- <sup>19</sup>S.S. Chang and A.B. Bestul, *J. Chem. Thermodyn.* **6**, 325 (1974).
- <sup>20</sup>C.T. Moynihan, A.J. Easteal, J. Wilder, and J.C. Tucker, *J. Phys. Chem.* **78**, 2673 (1974).
- <sup>21</sup>C.A. Angell, in *Supercooled Liquids*, edited by J.T. Tourkas, D. Kivelson, U. Mohanty, and K.A. Nelson (American Chemical Society, Washington, D.C., 1997), pp. 14–27.
- <sup>22</sup>G. Adam and J.H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
- <sup>23</sup>C.A. Angell and W. Sichina, *Ann. (N.Y.) Acad. Sci.* **279**, 53 (1976).