

# Effect of pressure on the fragility parameter: A density scaling point of view and its recent modification

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## **Abstract:**

The isobaric fragility parameter of typical supercooled van der Waals liquids and polymer melts usually decreases with increasing pressure. This known finding constitutes an important criterion of validity for the models formulated to describe temperature-pressure or temperature-density dependences of structural relaxation times and viscosities of glass-forming materials. For instance, the temperature-pressure entropic model originally proposed by Avramov required modifying [1] to correctly predict the pressure dependence of the isobaric fragility. However, the density scaling law for molecular dynamics near the glass transition, which has been intensively studied in the last decade, gives [2] an important insight into the fragility concept based on the short-range effective intermolecular potential and elucidates the observed pressure behavior of the fragility parameter. Exploiting the isobaric and isochoric fragility parameters, we show that the pressure changes in the isobaric fragility depend on the pressure changes in the product of the isobaric expansivity and the glass transition temperature if the power law density scaling is valid. We arrive at this result by presenting the evidence that the isochoric fragility is independent of thermodynamic conditions in the power law density scaling regime [2]. The proper pressure dependence of the isobaric fragility is also predicted [3] by two models of the temperature-volume dependence of structural relaxation times and viscosities. We compare these predictions. Finally, we discuss the peculiar behavior of the isobaric fragility under high pressure observed in supercooled associated liquids. We show that the density scaling exponent is not only a new measure of the relative contribution of temperature and density to the molecular dynamics near the glass transition, but it also can be a measure of the degree of hydrogen bonding if the density scaling law is modified to reflect complex dynamics of H bonds [4].

## **References:**

- [1] I. Avramov, A. Grzybowski, and M. Paluch, *J. Non-Cryst. Solids* 355, 733 (2009).
- [2] G. Floudas, M. Paluch, A. Grzybowski, and K. Ngai, *Molecular Dynamics of Glass-Forming Systems: Effects of Pressure*, Chap. 2, Springer-Verlag Berlin Heidelberg 2011.
- [3] E. Masiewicz, A. Grzybowski, A. P. Sokolov, and M. Paluch, *J. Phys. Chem. Lett.* 3, 2643 (2012); R. Casalini, U. Mohanty, and C. M. Roland, *J. Chem. Phys.* 125, 014505 (2006).
- [4] S. Pawlus, M. Paluch, and A. Grzybowski, *J. Chem. Phys.* 134, 041103 (2011)