



Received: 28-08-2024
Accepted: 08-10-2024

International Journal of Advanced Multidisciplinary Research and Studies

ISSN: 2583-049X

Discussion of Two Models for the Glass Transition Temperature

John H Jennings

M.S. 2530 Hillegass Ave. #307 Berkeley, CA 94704, USA

DOI: <https://doi.org/10.62225/2583049X.2024.4.5.3343>

Corresponding Author: John H Jennings

Abstract

In Bovey/Winslow (1979) ^[1] pp. 366-367, there are presented $d T_g / d P$ according to Goldstein (1963) ^[2]: $d T_g / d P = (\beta_l - \beta_g) / (\alpha_l - \alpha_g)$ or O'Reilly (1962) ^[3]: $d T_g / d P = TV (\alpha_l - \alpha_g) / \Delta C_p$. O'Reilly presented a TABLE showing how the second equation agrees with the experiment and that will be included here. Goldstein maintains that the two

expressions are equal, but Fanggao, *et al* (1996) ^[4] say that O'Reilly is correct while Goldstein gives values that are "appreciably higher" than $d T_g / d P$ at the glass transition. This paper will examine Goldstein's derivation to ascertain why BOVEY/WINSLOW says $(\beta_l - \beta_g)$ is a questionable quantity.

Keywords: Bovey/Winslow Goldstein O'Reilly Fanggao "Glass Transition Temperature in Polymer"

Introduction

In Abstract, I outlined the comparison of Goldstein and O'Reilly for the glass transition temperature in polymer, T_g , dependence on P . They differ because Goldstein, in his article, equates them with "if $d V_e = 0$ implies $d S_e = 0$, we find $(\beta_l - \beta_g) / (\alpha_l - \alpha_g) = TV (\alpha_l - \alpha_g) / \Delta C_p$ ". This is on page 3370 of Goldstein's article. Also, it is incorrect, as Fanggao (1996) ^[4] says on page 432: "the values of $\Delta k / \Delta \alpha [= (\beta_l - \beta_g) / (\alpha_l - \alpha_g)]$ are appreciably higher than those of $d T_g / d P$ [correction] at the glass transition."

Results

Here we present Bovey/Winslow (1979) ^[1]'s TABLE. It is the following, from page 367.

Table 6.3: Difference of T_g on P , showing Agreement with Eq. (6.49)

Polymer	dT_g / dP ($^{\circ}C / atm$)	$TV \Delta\alpha / \Delta C_p$ ($^{\circ}C / atm$)
Polyvinyl acetate	0.022	0.025
Polyisobutylene	0.024	0.024
Polyvinyl chloride	0.016	0.030
Glycerol	0.004	0.004
n-propanol	0.007	0.005
Selenium	0.013	0.011
Salicin	0.005	0.005
B ₂ O ₃	0.020	0.027

Here is (6.49), from (O'Reilly JM, 1962) ^[3], (2).

$$dT_g / dP = TV \Delta\alpha / \Delta C_p.$$

The glass transition temperature is described as the outcome of the above formula, the Kesom-Ehrenfest relation (Leuzzi/Nieuwenhuizen 2008, page 49), which is derived in (Goldstein 1963) ^[2] for $d S_e = 0$, but for $d V_e = 0$ Goldstein is incorrect as explained.

Conclusions

Here, the author is briefly enabling the reader to ascertain the significance of $d T_g / d P$ for glass transition temperature. However, the only thing I've been able to mention about why BOVEY/WINSLOW says $(\beta_l - \beta_g)$ is a questionable quantity is that it seems odd that $(\beta_l - \beta_g)$ would occur in a derivation such as this. Otherwise, it is clear that the TABLE is for O'Reilly alone and is correct.

References

1. Bovey FA, Winslow FH. *Macromolecules: An Introduction to Polymer Science*. Academic Press New York, 1979.
2. Goldstein M. Some Thermodynamic Aspects of the Glass Transition: Free Volume, Entropy, and Enthalpy Theories. *The Journal of Chemical Physics*. 1963; 39:3369-3374.
3. O'Reilly JM. The Effect of Pressure on Glass Temperature and Dielectric Relaxation Time of Polyvinyl Acetate. *Journal of Polymer Science*. 1962; 57:429-444.
4. Fanggao C, Saunders GA, Lambson EF, Hampton RN, Carini G, Di Marco G, Lanza M. Temperature and Frequency Dependencies of the Complex Dielectric Constant of Poly (ethylene oxide) under Hydrostatic Pressure. *Journal of Polymer Science: Part B: Polymer Physics*. 1996; 34:425-433.
5. Leuzzi L, Nieuwenhuizen TM. *Thermodynamics of the Glassy State*. Taylor & Francis, 2008.