



Non-equilibrium thermodynamics of glassy polymers: Use of equations of state to predict gas solubility and heat capacity



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ABSTRACT

The use of Non-Equilibrium Thermodynamics for Glassy Polymers (NET-GP) model to predict infinite dilution gas solubility coefficient is revised in this work and its extension to the analysis of apparent constant pressure heat capacity in polymeric materials below the glass transition temperature T_g is developed. Use is made of different Equations of State (EoS), in the class of tangent-hard-spheres-chain theories, to predict the thermal expansion coefficient below T_g , resulting in consistent representations of the Henry's coefficient for gaseous species in the same temperature range, for the case of different versions of Statistical Associating Fluid Theory (SAFT) EoS. With reference to calorimetric properties, the analysis here performed indicates that NET-GP endowed with EoS tuned on melt phase equilibrium properties does not allow for the prediction of the bulk modulus of the glassy polymeric phase, and only qualitative behavior for the apparent heat capacity are reproduced. On the other hand, after the use of experimental data from structural relaxation experiments to evaluate the bulk modulus in glassy state, a satisfactory prediction of the excess heat capacity is obtained within the same framework, for the case of different non-equilibrium conditions. Conclusion are finally drawn for the need to account for additional order parameters in NET-GP approach in order to address the representation of the complex calorimetric behavior exhibited by glassy polymeric materials.

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1. Introduction

Understanding the nature of glass transition phenomenon which characterizes the behavior of most of the polymeric materials is of major importance from the heuristic point of view, and the description (and prediction) of the non-equilibrium value of thermodynamic properties below the glass transition point is crucial to the analysis of performances of several products and processes in which glassy polymeric materials are of relevance. Although many efforts have been devoted in the past fifty years to elaborate a general representation of the characteristics of the glass transition in polymeric and non-polymeric materials, the debate about its nature is still open. Noticeable contributions have been given both from the perspective the formation of glass is a pure kinetic process [1,2], and from that

accounting for a thermodynamic transition as responsible for the variation of system properties across the region between glassy and melt states [3,4]. In view of the complexity of the problem, most of the efforts to derive relations for the estimation of thermodynamic and transport properties below the glass transition temperature are empirical in character. Among these, NET-GP, introduced by Doghieri and Sarti almost twenty years ago [5], is a simple approach allowing for the direct extension to non-equilibrium glassy states of the description of thermodynamic properties that an arbitrary equation of state for amorphous phases provides for the case of melt states. NET-GP approach moves from the assumption that a glassy phase is frozen into non-equilibrium conditions for purely kinetic reasons, and it makes use of polymer mass density as measurement of the out-of-equilibrium degree of the system. In the past two decades NET-GP model has been successfully applied to the correlation and prediction of solubility of gases and vapors in glassy polymers in several works [6–8]. The model proved to satisfactorily account for the relevant effect of excess free

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volume on gas vapor solubility and on solubility selectivity for the case of mixed gas or mixed vapor sorption processes in glassy polymers. The effect of annealing/swelling pretreatments on the solubility property of the glassy polymeric materials was also effectively represented by the model, through the different value of the dry polymer mass density produced by the specific protocol used. In a recent development of the model, also the volume dilation induced in polymer samples by the sorption of swelling components is directly accounted for [9]. The predictive ability of the model was extended this way to the phase equilibria solution for glassy polymeric system at high gas pressure of high vapor fugacity, as well as to the case of analysis of liquid-liquid-equilibria.

The work here presented focuses on the case of pure polymer properties, and the role in NET-GP procedure of thermodynamic properties of equilibrium states underlying the glassy condition is specifically addressed. To this aim, use is made of different equations of state, endowed within the NET-GP framework, leading to the description of calorimetric properties. This work aims to contribute to the discussion, about the characteristics of hypothetical equilibrium properties for polymeric species below T_g . The latter is indeed an essential step along the way to the development of more comprehensive predictive tools for thermodynamic properties of non-equilibrium polymer glassy phases.

Furthermore, the results obtained in this work recognizes the limits of the current version of NET-GP model, which ultimately results from the nature of the only order parameter used. Indeed, to account for the out-of-equilibrium degree of the glassy phase the model counts on the volume per polymer mass, which is actually a directly measurable quantity. More specifically, the NET-GP does not stand on the condition of a fixed value of the order parameter in the whole range of glassy state, as the latter rather depends on current and past values of the externally controlled variables. In this respect, it should be emphasized that the approach differs from the well-known idea of fictive temperature as order parameter used to the same purpose [10], both in its basic statements and results. In fact, the use of volume deformation of polymer network as order parameter ultimately brings to different relations for thermodynamic property in glassy state, with respect to the approach based on the fictive temperature idea. A direct comparison of the description of glassy polymer properties attained through NET-GP and other approaches will not be attempted in this work, and the model here analyzed will be rather taken as a zero-order approximation of the parametric description of out-of-equilibrium condition for a polymer system.

In this view, the fundamental relations for NET-GP approach are first briefly revised in the following section, aiming at illustrate and briefly analyze the details of the assumptions made. Section 3 of the paper focuses on the NET-GP analysis of the infinite dilution gas solubility coefficient, and its variation in a temperature range across the glass transition point. Specific expressions are thus derived to link Henry's coefficient to the equilibrium properties of the polymer/solute mixture and to the apparent thermal expansion coefficient for the pure polymeric species below the glass transition temperature. Relations derived refer to the use, in the NET-GP framework, of an arbitrary EoS, which provides the explicit expression for the residual Helmholtz free energy density as function of temperature and component species densities. Stated relations are thus suitable to be used with any equation of state in the class of tangent-hard-spheres-chain or lattice fluid theory.

A specific aim of this paper is the extension of NET-GP approach to the analysis of apparent heat capacity in isobaric cooling or heating runs in glassy polymeric systems. The proper equations relating the excess heat capacity to equilibrium bulk

modulus and non-equilibrium thermal expansion coefficient, within NET-GP assumption, are then here derived in Section 4. The expression for apparent bulk modulus in structural relaxation processes is also obtained in the same thermodynamic framework. This analysis is not meant to derive a new model for heat capacity in glassy polymers, but rather to explore the capability and the limits of the non-equilibrium thermodynamic tool, already well established for different purposes, through its straightforward application to the analysis of calorimetric properties. For this reason, no effort is made to compare results from NET-GP model with those obtained by means of other specific tools for the prediction and correlation of thermal properties in glassy polymers. In view of the discussion which follows, however, it is worthwhile to mention here the best known result for the correlation between calorimetric and volumetric property jumps at the glass transition, which can be derived after the general assumption the glassy state is described through the use of one order parameter, in turn set to a constant value throughout the glassy region. Under those conditions, the results are derived for a unit value of the Prologine-Defay ratio Π [11]:

$$\Pi \equiv \frac{(\Delta C_p / \Delta \alpha)}{(T_g \Delta \alpha / \Delta \kappa) / \rho_{pol}^{(g)}} = 1 \quad (1.1)$$

where ΔC_p , $\Delta \alpha$ and $\Delta \kappa$ are glass transition jumps for specific heat capacity, thermal expansion coefficient and isothermal compressibility, respectively, while $\rho_{pol}^{(g)}$ and T_g indicate polymer mass density and temperature at the transition. It should be emphasized that the above result is also consistent with the Ehrenfest equations [12], which, in turn, are derived after the assumption the evolution from melt to rubbery state can be interpreted as second order thermodynamic transition.

The use of NET-GP in association with different EoS both in the analysis of infinite dilution gas solubility coefficient and excess heat capacity is exemplified analyzing the behavior of few conventionally glassy polymers for which suitable experimental data are available from the literature (Section 5). Because of the solid thermodynamic ground they are based on, and in view of the successes obtained through their use in the description of thermodynamic properties in amorphous phases [13–15], different Equations of state in the class of hard-spheres-chain theory have been considered. Model calculations have been performed after the alternative use of two distinct versions of Statistical Association Fluid Theory and one version of Perturbed Hard Sphere Chain Theory for the description of thermodynamic properties at the equilibrium conditions underlying the glassy states in glassy polymers. The problem of identifying the proper EoS for the representation of equilibrium properties below the glass transition point raises a non-trivial question in the use of NET-GP approach. Indeed, as the general EoS models cannot be simply tuned to provide the best representation of equilibrium properties in the conditions of interest, and the calculation necessarily relies on the extrapolation of such properties down to temperatures below the glass transition, typically after the best fit of data available in melt phase. In this work, the results from the use of different EoS will be compared to discuss the effect of different thermodynamic properties predicted for hypothetical equilibrium states of polymeric materials below the glass transition temperature.

2. . NET-GP approach

The essential assumption in NET-GP approach to the description

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