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Predictive model for gas and vapor solubility and swelling in glassy polymers I: Application to different polymer/penetrant systems

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ABSTRACT

An extensive analysis is performed for the use of a model recently introduced for sorption induced volume dilation in glassy polymers, which can be combined with the nonequilibrium lattice fluid model (NELF) for the description of gas and vapor solubility in glassy polymers in a wide temperature range below the glass transition, from dry to fully plasticized conditions. The procedure extends the capability of previous versions of NELF model, as it refers to correlation and prediction of solubility of vapors and swelling agents. To this aim, the model counts on an additional out-of-equilibrium parameter for the polymeric species that interprets its pseudoequilibrium compressibility, and it can be retrieved from the analysis of pure component pressure–volume–temperature data below T_g. The examples discussed in this work show that the overall procedure is highly reliable and addresses the key properties of the system for the direct interpretation of the effect of temperature, solute fugacity and state of glassy polymers on pseudoequilibrium volume swelling and solute content.

1. Introduction

Several reliable tools are available for the representation of thermodynamic properties of amorphous polymer/solute mixtures above the glass transition temperature, which can be used confidently for correlations and predictions of vapor liquid equilibrium (VLE) behaviors. Among these, leading roles are taken now by volumetric equation of state models (EoS), as Lattice Fluid [1–3] or Hard Sphere Chain Theories [4–6]. In last decades, indeed, EoS relations have been successfully applied to the description of binary, as well as multicomponent VLE and LLE conditions, and they are now essential parts of any process simulation tool that deals with polymer solutions in melt phase. On the other hand, the analysis of phase equilibria in glassy polymeric systems is often limited to a posteriori correlations by means of empirical tools [7–9], or to semiempirical models treating the glassy systems as elastic solids [10,11], or in the framework of the free volume theory [12]. The difficulties in the representation of thermodynamic behaviors below T_g are mostly associated to the nonequilibrium nature of these systems, for which the usual set of state variables for amorphous phases is not sufficient to identify unambiguously all meaningful properties. Indeed, it is well known that, according to the specific preparation protocols for the polymeric samples, in terms of cooling rate, annealing or preswelling treatment, the apparent solubility of gas or vapor species may be different for the case of same polymeric matrix at assigned value of temperature, pressure and solute fugacity [13,14]. Among the attempts to describe the out-of-equilibrium conditions of glassy solute/polymer systems, the NELF model introduced by Dogheri and Sarti [15] in 1996, proved to be successful in the representation of gas and vapor solubility in conventional glassy polymers and blends, also accounting for the effect of thermal and sorption history of the sample. The model counts on the use of the pseudoequilibrium polymer mass density as additional state variable, and it makes use of this parameter as a proper measurement of the out-of-equilibrium degree in the system. As it refers to the evaluation of the effect of temperature and species mass density on the free energy and solute chemical potential in the glassy system, the basic assumption of the NELF model is that the same expressions developed for equilibrium EoS above T_g can be applied. In fact, several different versions of the same model can be obtained with reference to the use of different EoS in this respect. While the acronym NELF for the model reminds of the use of a lattice fluid theory for the equilibrium properties in the first implementation of the procedure, its application was later extended to the use of other equation of state, such as the Perturbed Hard-Sphere-Chain (PHSC) and the Statistical Associating Fluid Theory (SAFT). This led to the development of the corresponding nonequilibrium models

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[16,17], often referred as the nonequilibrium thermodynamics for glassy polymers (NET-GP). In all its versions, the pseudoequilibrium solute content at assigned thermal and chemical potential was thus calculated from the NELF model for the specific glassy sample after accounting for independent information about polymer mass density, at the condition of interest. Many examples of the application of the NELF model to the solubility of both single and mixed gas in glassy polymeric matrixes proved the reliability of the procedure and the validity of the use of polymer mass density as order parameter for the nonequilibrium conditions [18–23]. The knowledge of the volume per polymer mass of the system at pseudoequilibrium conditions is a pre-requisite in NELF procedure, and it has been representing a limit for its use as a predictive tool. However, the analysis of suitable relations for the out-of-equilibrium parameter as function of thermodynamic potentials has constantly been in order, since it was introduced. A specific approach has been recently proposed in this respect by Minelli and Doghieri, aiming at the evaluation of pseudoequilibrium polymer density in the mixture solute/polymer of interest below T_g [24]. This model requires the use of a limited number of pure polymer out-of-equilibrium properties, which, in turn, can be retrieved from the analysis of conventional pressure–volume–temperature (pVT) data in the glassy region. An extensive analysis is performed in this work to show the reliability of the resulting predictive procedure for gas and vapor solubility as function of temperature and solute fugacity in glassy systems, up to the condition of glass-to-rubber transition. For the sake of simplicity, the analysis is here limited to the case of conventional protocols for the preparation of glassy polymer samples, so that solubility and volumetric data from different literature sources could be combined in order to comprehensively describe the thermodynamic properties for the systems of interest. A second part of the work will be then devoted to the analysis of the effect of specific thermal or pre-swelling history on the thermodynamic properties of the polymer/solute mixture, which will be pursued by accounting for the same relation between volumetric and solubility properties in out-of-equilibrium conditions. The remarkable reliability of the procedure described in this work discloses the way to the development of a general predictive tool for gas and vapor solubility in glassy polymers, both for binary and multicomponent systems, from dry to fully plasticized conditions, based on a comprehensive characterization of pure polymer volumetric properties, above and below the glass transition temperature. This kind of tool will be precious in the analysis and design of a number of processes in which VLE problems in glassy systems are relevant, from vapor sensors to gas separation membranes [25,26], from packaging applications [27] to drug delivery devices [28].

2. Model

In this section, a brief description is given of fundamental assumptions and relations used by the NELF model to represent gas and vapor solubility and swelling behavior in glassy polymers. The basic features and input variables in the original NET-GP approach will be first introduced, then the key points in the model for volume dilation in sorption conditions will be addressed. Finally, the list of material parameters necessary to the representation of thermodynamic properties will be analyzed in details, for the case in which the lattice fluid theory is specifically considered to the description of equilibrium conditions. Although reference to more general cases would not be difficult, we will here consider the case of a polymeric mixture of N_s solute components (index i: $1 \le i \le N_s$) and one polymeric species (index $i = N_c = N_s + 1$).

2.1. Approach of NET-GP

The nonequilibrium thermodynamics of glassy polymers (NET-GP) approach was introduced for the first time in 1996 by Doghieri and Sarti [15], and then discussed in several papers since then [18–23,29,30]. It actually represents a semi-empirical approach toward the extension to nonequilibrium states below T_g of any arbitrary equation of state model for the equilibrium properties of solute/polymer amorphous mixtures. Indeed, the same approach it can be applied to any EoS for a polymeric mixture of N_c components that allows to obtain suitable expressions for the equilibrium Helmholtz free energy density, a^{Eq}, as function of temperature T and species mass density ρ_i of all solute components $(1 \le i \le N_s)$ and polymeric species $(i = N_c)$:

$$a^{Eq} = a^{Eq}(T, \{\rho_i\}_{i=1,N_c}) \tag{1}$$

The NET-GP approach relies on the assumption that the mass density of the polymeric species in the mixture (ρ_{pol}) is the proper order parameter for the description of the out-of-equilibrium degree for the system at assigned temperature T, pressure p and mass ratio for solute components Ω_i $(1 \le i \le N_s)$. The proper arguments of nonequilibrium Helmholtz free energy density function can thus be presented as follows:

$$a^{NE} = a^{NE}(T, p, \{\Omega_i\}_{i=1,N_s}, \rho_{pol}) \tag{2}$$

After the specific assumption that the mass density of the polymeric species in the mixture behaves as internal state variable for the system (i.e. its rate of change in time is a function of the same set of variable describing the nonequilibrium state), simple relations are derived for thermodynamic properties in nonequilibrium conditions [15]. In view of their relevance for the phase equilibrium problems, we recall here those referring to chemical potential μ_i of solute components:

$$\mu_i^{NE} = \mu_i^{NE}(T, p, \{\Omega_j\}_{j=1,N_s}, \rho_{pol}) = \mu_i^{Eq}(T, \{\rho_j\}_{j=1,N_c}) \quad 1 \le i \le N_s \tag{3}$$

The simple result in Eq. (3) allows the straightforward extension to nonequilibrium states of the expression for chemical potential of solute species obtained after corresponding equilibrium EoS for pertinent variables temperature and component densities.

It is useful to briefly recall the peculiar characteristics of the formulation of phase equilibrium conditions within the NET-GP theory, which could be used for the estimation of solute content in the glassy mixture at pseudoequilibrium, compared to those of the corresponding problems at equilibrium conditions. Indeed, while the expressions for chemical potential of solute species as function of species mass density are the same developed in equilibrium theories, the pseudoequilibrium value of mass densities for the polymeric species cannot be calculated from the corresponding equation of state, but it requires to be directly input in the model after its estimation from independent information.

2.2. Model for volume dilation

In several previous works, in order to use the NET-GP model for gas solubility calculation in glassy polymers, the mass densities of the polymeric species at pseudoequilibrium conditions was often assumed to be equal to the value measured for dry polymer at the same temperature (ρ_{pol}^0) [29,31]. In fact, the latter assumption is suitable for the evaluation of solubility in glassy polymers for the case of non-swelling agents (low critical temperature permanent gases), and also for that of vapors, when limited to the conditions of infinite dilution of solute species in the polymer matrix. Conversely, when dealing with the estimation of high-pressure solubility of swelling gas or of vapor components at non-vanishing fugacity, the NET-GP model was used, in early applications, by accounting for a