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Modelling sorption induced volume dilation in glassy polymers within the NET-GP approach

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ABSTRACT

Two distinct approaches proposed in the literature for the description of sorption induced volume dilation in glassy polymers are discussed and compared with respect to their predictive capability. Both Non-Equilibrium Restrained Swelling model (NE-RS) and Dry Glass Reference Perturbation Theory (DGRPT) have been proposed to address this problem within the framework of Non-Equilibrium Theory for Glassy Polymers (NET-GP). Both qualitative and quantitative characteristics of results from the two models are considered and corresponding predictions are compared with experimental data available in the literature, for the case of sorption of gas or vapor penetrants in conventional glassy polymers. Conclusions are drawn about the crucial role of correct description of induced volume swelling in prediction of high-pressure gas solubility in glassy polymers through NET-GP approach, as well as about different abilities and limits of the two models so far proposed to this aim.

1. Introduction

The capability of predicting mass uptake and volume change of polymeric materials exposed to fluid phase at assigned fugacity of penetrant components is of paramount importance in a number of different processes and applications, from membrane optimization for gas separation or organic solvent nanofiltration, to the design of gas sensors or drug delivery systems. Understanding fundamental thermodynamic characteristics of swollen polymeric phases, in turn, is a necessary prerequisite to identify the proper model approach to the discussion of phase equilibrium problems in polymeric systems. It can be easily recognized that well established tools for the description of equilibrium properties can be confidently used in this respect for the case of polymeric materials above the glass transition temperature. Indeed, several equations of state (EoS) approaches proposed in the literature [1–4] proved to be effective in predicting both volume change and mass uptake in melt or rubbery polymers exposed to gas or vapor phase, from infinite dilution condition to the case of high fugacity/activity for the penetrant components. Among Equation of State models specifically developed to describe thermodynamic properties of polymeric phases, one of the first to appear is the Perturbed Hard Sphere Chain Theory, proposed by Prausnitz [5], to which Fermeglia significantly contributed, also through the set-up of molecular dynamic tools for the retrieval of corresponding parameters [6].

To the scope of this work, it is useful to put in evidence that for the case of polymer-solute mixtures at low or medium solute content, when specific interactions are absent, substantially composition independent values are measured for solute partial specific volume in the mixture, as well as for the solubility coefficient. The same condition holds, consequently for volume swelling coefficient, meant as the ratio between relative volume change of the system and solute fugacity in the mixture. The latter case is, for example, well documented in a work by Freeman [7], in which both mass change and volume change of PDMS samples have been measured at different temperatures, for samples exposed either to methane and to *n*-butane at low and medium pressure values.

In fact, when approaching the same analysis for polymeric systems below the glass transition temperature, the problem is faced that the equilibrium tools cannot be applied directly, in view of the non-equilibrium nature of glassy systems. In addition to that, we deal with sensitivity of sorption coefficient and swelling coefficient to solute concentration which are qualitatively different from those observed for the same kind of systems above Tg.

Several models have been considered in the past forty years to address the question of proper thermodynamic description of out-of-equilibrium glassy systems, among which are polymeric mixtures below the glass transition temperature [8–13]. On the other hand, one is the approach which proved to be successful in extending the description established for equilibrium states in polymer-solute mixtures to the

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non-equilibrium conditions below the glass transition temperature. This is the Non-Equilibrium Theory for Glassy Polymers (NET-GP) [14]. The latter assumes that the polymer mass density can be regarded as a suitable order parameter to describe out-of-equilibrium conditions, and that it can be treated as an internal state variable of the system. Once an appropriate expression for the equilibrium Helmholtz free energy density is formulated as a function of temperature and of mass densities of all components, the solute chemical potential can be evaluated within the NET-GP framework, provided that independent information on the polymer mass density at the relevant pseudo-equilibrium states is available. The NET-GP methodology was initially applied to Sanchez and Lacombe's compressible lattice fluid theory [1,2], leading to the development of the Nonequilibrium Lattice Fluid (NE-LF) model [14, 15]. Subsequently, this approach was extended and connected to several equations of state, including those belonging to the class of Statistical Associating Fluid Theory (SAFT) [3,16,17].

Different from the straightforward application of the corresponding equilibrium model, the NET-GP framework requires the additional knowledge of polymer density under pseudo-equilibrium conditions. This specific information, when not available from direct measurement, can be only derived after a detailed characterization of the volumetric behaviour of the polymeric mixture of interest. In the typical condition of interest here, the dry polymer mass density at the process temperature can be measured directly or estimated from glass transition temperature and thermal expansion coefficient at glassy state. After the information about dry polymer mass density, the application of NET-GP approach allows to reliably calculate the solubility coefficient of gases and vapours at infinite dilution conditions [18]. In order to extend the analysis to medium and high solute concentration values, a link between polymer mass density to either solute mass fraction or solute fugacity is required. Two approaches have been effectively proposed so far in the literature to provide the closure of this specific problem: the Non-Equilibrium Restrained-Swelling (NE-RS) [19] model and the Dry Glassy Reference Perturbation Theory (DGRPT) [20]. They offer two different routes to relate volume swelling of polymeric systems below the glass transition temperature to the corresponding mass uptake for samples exposed to fluid phase at assigned fugacity of gas or vapor penetrant components.

Their assumptions are briefly presented in the following sections and the results of their application to the description of gas and vapor sorption/dilation isotherms is discussed with reference to the case of conventional glassy polymer, for which pure polymer equilibrium volumetric data are known, so that the pertinent equation of state is defined in specific term, and EoS model can be ultimately applied in effective predictive terms.

While any equation of state for compressible polymer solute mixtures can be considered for the application of NET-GP approach, the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) is here adopted, consistently with the choice taken in most recent examples of application of the two models presented in the literature.

Discussion of the calculation routes proposed within NE-RS and DGRPT is preceded, in what follows, by a brief presentation of experimental evidence about the relation between volume dilation coefficient and solute content and solute fugacity. Indeed, the two models move from alternative interpretation of these kinds of data.

2. Experimental evidence for sorption induced volume swelling in glassy polymers

In situ direct measurement of volume swelling for polymer samples induced by gas or sorption are difficult to take and only a limited amount of data of this kind is reported in the literature. In addition to that, results from this kind of measurement are typically affected by larger uncertainty with respect to mass uptake and, for what refers to glassy polymeric systems, the possible effect of preparation protocol of the sample should be kept in mind, as well as that of different constraint, such as for free film with respect to supported coatings.

Notwithstanding all limitations mentioned above, few elements can be recognized in features of sorption induced volume swelling in glassy polymers from the available experimental data [21–28]. Figures below illustrate examples of experimental evidence, reported in the literature, for gas sorption induced volume change, as function of gas fugacity (Fig. 1), and for relative volume change induced by vapor sorption, as function of vapor activity (Fig. 2). For the sake of simplicity of the analysis and the discussions, collection of examples presented in the two figures is limited to the case of systems in which specific interactions, such as those resulting from H-bonds, are absent. Data in Figs. 1 and 2 include the cases of conventional glassy polymers (PC, PMMA, PEMA), characterized by relatively low glass transition temperature and excess free volume, and those of super-glassy polymers (PIM-1 and PTMSP) which are endowed with very high excess free volume at room temperature, as result of their extremely high Tg values. Data in Fig. 1 reveals that volume dilation induced by sorption of light gases is typically proportional to gas fugacity, both for conventional and super glassy polymers, thus producing a swelling coefficient, calculated as ratio between relative volume change and solute fugacity substantially independent on solute concentration. The significance of the latter observation is made clear when it is considered that, on the opposite, the solubility coefficient is largely decreasing with solute content in the same concentration range. Data in Fig. 2 reveals that it is difficult to recognize a similar trend for the general case of vapor sorption in glassy polymers, although the rule is obeyed by data measured for volume change of PC sample induced by sorption of acetonitrile vapor up to significant activity value. Data of volume change for most of the systems considered for Figs. 1 and 2 are finally reported in Fig. 3 as function of relative mass uptake of polymer samples in the gas or vapor sorption experiment. Analysis of data in Fig. 3 put in evidence that the partial specific volume of gas or vapor component in the glassy polymer phase significantly increases, in all cases, when solute concentration increases. The latter feature is particularly evident for the case of vapor sorption in super glassy polymers, for which the infinite dilution partial specific volume of the solute component appears to be negligible. In more specific terms, it can be observed that partial specific volume of vapors in glassy system at high vapor activity is of the same order of pure component specific volume in condensed state, while the infinite dilution partial specific volume results to be orders of magnitude lower. For the case of gas sorption in conventional glassy polymers, on the other hand, while the qualitative trend is similar, an appreciable value of the partial specific volume of the gas is derived at infinite dilution condition, still much lower than the expected value for specific volume of corresponding pure component in condensed state.

3. Modelling gas and vapor sorption in glassy polymers

The Nonequilibrium Theory for Glassy Polymers (NET-GP) assumes that the chemical potential of a solute in a glassy state is equivalent to the chemical potential in a hypothetical equilibrium (μ_s^{EQ}) state at the same temperature (T), composition (ω), and polymer density $\left(\rho_{pol}\right)$ [14]:

$$\mu_s^{NE}\left(T,p,\omega,\rho_{pol}\right)=\mu_s^{EQ}\left(T,\omega,\rho_{pol}\right) \quad (1)$$

Because the equilibrium volumetric equation of state does not apply to glasses, an additional relation for the polymer density (or specific volume) is required to solve for the pseudo equilibrium condition.

To this aim, either equations which correlate pseudo-equilibrium volume per polymer mass $\left(V_{tot}/m_p\right)$ in the system to the solute mass ratio $\Omega_s$or the solute fugacity $f_s$could be used. The first kins of relations refers to expressions for the solute partial specific $\overline{V}_S$ in the polymeric mixtures, while the second kind directly points at representing the

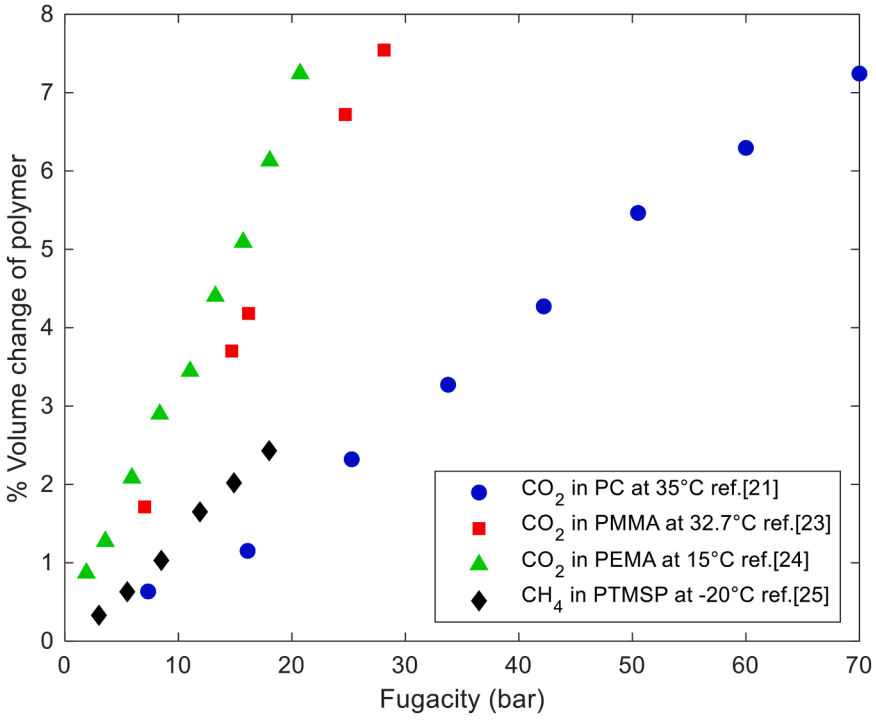

Fig. 1. experimental data from technical literature for gas sorption induced volume change in glassy polymer samples as function of gas fugacity.

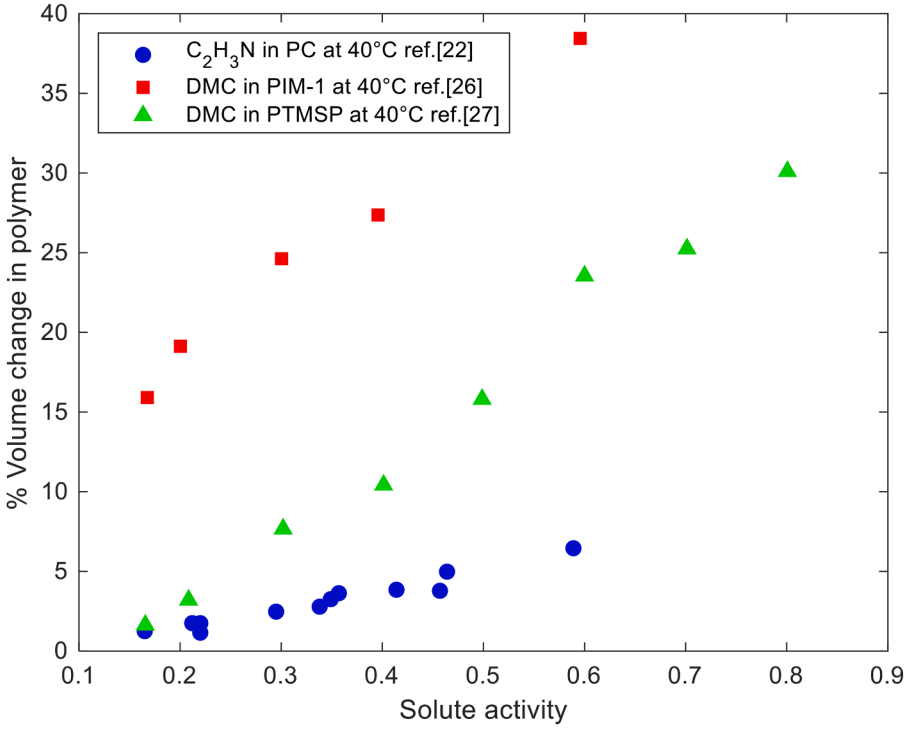

Fig. 2. experimental data from technical literature for vapor sorption induced volume change in glassy polymer samples as function of vapor activity.

swelling coefficient k_{sw}. Both terms can be easily calculated after the dependence of polymer density over solute density at pseudo-equilibrium conditions:

$$\overline{V}_S \equiv \left(\frac{d(V_{tot}/m_p)}{d\Omega_s}\right)_{T,p} = -\frac{1}{\rho_p}\frac{(d\rho_p/d\rho_s)_{T,p}}{1-(d\rho_p/d\rho_s)_{T,p}} \tag{2}$$

$$k_{sw} \equiv \left(\frac{1}{V_{tot}}\frac{dV_{tot}}{df_s}\right)_{T,p} = \frac{(d\rho_p/d\rho_s)_{T,p}}{(d\rho_p/d\rho_s)_{T,p}-1}\left(\frac{d\Omega_s}{df_s}\right)_{T,p} \tag{3}$$

In next sections strategies are described for the closure of phase equilibrium in NET-GP approach as suggested by DGRPT model, in which a relation of $\overline{V}_S$is considered, and by NE-RS model, which rather relies on assumptions about k_{sw}.

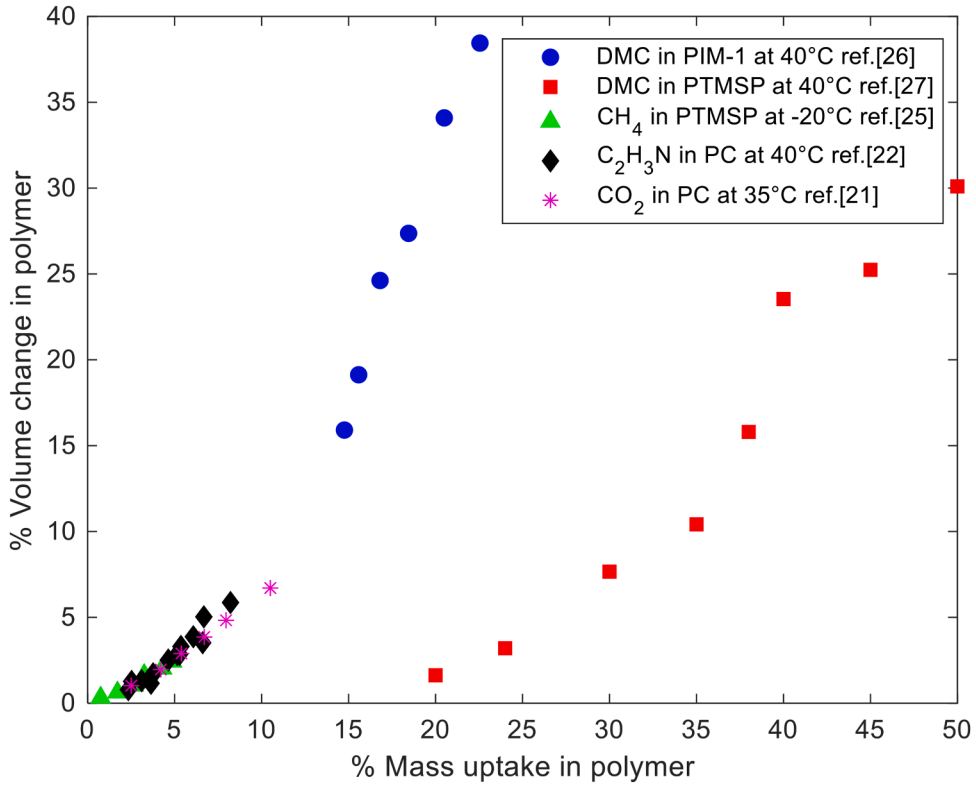

Fig. 3. experimental data from technical literature for gas/vapor sorption induced volume change in glassy polymer samples as function of mass uptake.

3.1. *The fundamental NE-RS equations*

The non-equilibrium restrained swelling (NE-RS) model simplifies the spectrum of polymer relaxation times into a bimodal distribution of "soft" (short-term) and "hard" (long-term) elements. In a standard sorption experiment, only the short-term modes reach equilibrium with the environment, while the long-term modes remain "frozen" [19]. The total specific volume per unit polymer mass V_{pol} is expressed as a weighted average:

$$V_{pol} = \chi V_{pol}^{EQ}(T,p,f) + (1-\chi)V_g \tag{4}$$

Where χ is a weighting factor representing the fraction of "soft" elements. $V_{pol}^{EQ}(T,p,f)$is the specific volume the polymer would reach if it were in full thermodynamic equilibrium at the given temperature, pressure, and solute fugacity. $V_g$is a constant term representing the specific volume of the long-term relaxation elements, which depends on the thermal history of the sample.

The parameters required for this predictive model can be retrieved from the pure polymer's pressure-volume-temperature (pVT) properties. The weighting factor χ is determined by comparing the low-pressure apparent compressibility of the glassy polymer $\kappa_g(T)$ to its equilibrium compressibility $\kappa^{EQ}(T)$ over the glass transition point:

$$\chi(T) = \frac{\kappa_g(T)}{\kappa^{EQ}(Tg)} \tag{5}$$

Note that $\chi(T)$ is temperature dependent because compressibility varies with temperature; its value is reasonably higher the closer the considered temperature is to T_g. However, for simplicity, it has always been used as a constant in previous works [18–32].

Once χ is known, V_g is calculated from the specific volume of the dry glassy polymer at low pressure $V_{pol}^{0}(T,p\to 0)$

$$Vg(T) = \frac{V_{pol}^{0}(T,p\to 0) - \chi V_{pol}^{EQ^0}(T,p\to 0)}{1-\chi} \tag{6}$$

To find the pseudo equilibrium solute content (ω) and the resulting polymer volume (V_{pol}), the set of equations (5) is solved simultaneously, with the second equation being necessary when the temperature of dry polymer density obtained from an experimental measure (T_{ref}) is different from the temperature of the system (T) using the glassy polymer thermal expansion coefficient (α_g):

$$\begin{cases} \mu_s^{NE}(T,p,\omega,\rho_{pol}) = \mu_s^{EQ}(T,\omega,\rho_{pol}) \\ V_{pol}^{0}(T) = V_{pol}^{0}(T_{ref})\cdot\left[1+\alpha_g(T-T_{ref})\right] \\ V_{pol} = \chi V_{pol}^{EQ}(T,p,f) + (1-\chi)V_g \end{cases} \tag{7}$$

This combined approach allows for the prediction of volume swelling across the entire glassy range up to the plasticization point (the glass-rubber transition), without relying on adjustable parameters from sorption experiments. This method showed satisfying results for conventional glassy polymers [19,29,30], where all the thermodynamic parameters can be retrieved from equilibrium data in the rubber region of polymers. However, it has been little explored for the case of super glassy polymers, that degrade before reaching their glass transition temperature and are therefore not observable in an equilibrium condition. In this case, also the parameter χ can be only guessed as a fitting parameter, since the equilibrium compressibility of the material is unknown [18].

It should also be observed that the last equation in set (5) returns a volume change for the polymer sample which is just proportional to the volume change expected for the corresponding equilibrium condition of the system. As for systems in which there are no specific interactions, the latter is proportional to solute fugacity in a significant range of solute concentration, the same trend is predicted, for the glassy state, by the NE-RS model, in qualitative accordance with the experimental data presented in the previous section.

3.2. The fundamental of DGRPT

This model focuses on the chemical potential of the polymer in the glassy phase as a function of temperature, glass density, and penetrant concentration. Indeed, it extends the NET-GP concept by claiming that also the polymer chemical potential can be estimated, at pseudo-equilibrium conditions, as the derivative of the Helmholtz free energy density with respect to polymer mass density, at constant temperature and solute concentration.

Different from the case of NE-RS model, which links the pseudo-equilibrium polymer density to temperature and solute fugacity, DGRPT model works on expression of partial specific volume for solute component as function of temperature and species density, so that the value of system volume per polymer mass is finally obtained through the solution of the following problem:

$$\begin{cases} \left(\frac{d(V_{tot}/m_p)}{d\Omega_s}\right)_{T,p}^{PE} = \overline{V}_S(T,\rho_p,\Omega_s) \\ (V_{tot}/m_p)\big|_{\Omega_s=0} = \frac{1}{\rho_p{}^0} \end{cases} \tag{8}$$

In order to discuss the expression proposed for solute partial specific volume within DGRPT it is useful to remind here the corresponding expression which holds for polymer solute phases at equilibrium conditions. Indeed, accounting for the relation between polymer mass density and solute mass density in an isothermal isobaric path at equilibrium:

$$\left.\frac{d\rho_p}{d\rho_s}\right|_{T,p}^{EQ} = -\frac{\rho_s(\partial\mu_s{}^{EoS}/\partial\rho_s) + \rho_p\left(\partial\mu_p{}^{EoS}\big/\partial\rho_s\right)}{\rho_s(\partial\mu_s{}^{EoS}/\partial\rho_p) + \rho_p\left(\partial\mu_p{}^{EoS}\big/\partial\rho_p\right)} \tag{9}$$

The following relation is derived, after Eq.(2), for equilibrium solute partial specific volume:

$$\overline{V}_S = \frac{1}{\rho_p}\frac{\Omega_s\left(\frac{\partial\mu_s{}^{EoS}}{\partial\rho_s}\right) + \left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right)}{\left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_p}\right) + \Omega_s\left(\frac{\partial\mu_s{}^{EoS}}{\partial\rho_s}\right) + (1+\Omega_s)\left(\frac{\partial\mu_s{}^{EoS}}{\partial\rho_p}\right)} \tag{10}$$

For the case of glassy phases, different expressions of the partial specific volume were proposed in subsequent refinements of original DGRPT model.

In the so-called "linear" version of DGRPT model, on the other hand, a relation for polymer mass density and solute mass density at pseudo equilibrium condition is proposed, on a purely empirical basis, according to the constraint described by the following equation [20]:

$$\rho_p{}^{PE}(T,\rho_s):$$
$$\mu_p{}^{EoS}(T,\rho_s,\rho_p{}^{PE}) - \mu_p{}^{EoS}(T,0,\rho_p{}^0) - \left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right)^0\rho_s - \lambda\left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_p}\right)^0(\rho_p{}^{PE} - \rho_p{}^0) = 0 \tag{11}$$

Where $\rho_p{}^0$ indicates mass density of dry polymer, while $\left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right)^0$ and $\left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_p}\right)^0$ represent derivatives of chemical polymer of polymer species in the mixture at dry conditions.

Parameter λ in the above equation was actually set to value zero in the first version proposed for DGRPT model (hereafter referred to as "DGRPT v1"), while it was considered as variable in the range from 0 to 1 in the second version of the model (hereafter referred to as "DGRPT v2") [33].

Indeed, DGRPT v1 provides a route for a pure prediction of the solute induced volume swelling in glassy polymers, in which the only out-of-equilibrium order parameter is the dry polymer mass density of the glassy sample, while DGRPT v2 introduces the additional order parameter λ, which, in particular, proved to be essential to represent the sweeling in glassy systems endowed with limited free volume [33].

The closure condition for NET-GP provided by "linear" version of DGRPT model can be finally expressed as represented in the following relation

$$\begin{cases} \left(\frac{d(V_{tot}/m_p)}{d\Omega_s}\right)_{T,p}^{PE} = \frac{1}{\rho_p}\frac{\left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right)^0 - \left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right)}{\left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right)^0 - \left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right) + \lambda\left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_p}\right)^0 - \left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_p}\right)} \\ (V_{tot}/m_p)\big|_{\Omega_s=0} = \frac{1}{\rho_p{}^0} \end{cases} \tag{12}$$

Eq.(12) should be actually preferred to Eq.(11) in the representation of closure problem for the case of a swelling induced in a glassy polymer sample by the gradual increase of solute content. Indeed, multiple values solutions exist of actually non-linear Eq.(11) and not all them, of course, allow for continuous relation of polymer mass density as function of solute content.

A further version of DGRPT model was recently proposed in which condition for pseudo-equilibrium polymer density is re-formulated as follows [34]:

$$\rho_p{}^{PE}(T,\rho_s):$$
$$\mu_p{}^{EoS}(T,\rho_s,\rho_p{}^{PE}) - \mu_p{}^{EoS}(T,0,\rho_p{}^0) - \left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right)^0\rho_s - \frac{\gamma}{2}\left(\frac{\partial^2\mu_p{}^{EoS}}{\partial\rho_s{}^2}\right)^0\rho_s{}^2 = 0 \tag{13}$$

In which γ is an adjustable model parameter, which is typically characterized negative sign

The latter model will be hereafter indicated as "DGRPT v3" and the corresponding closure condition for NET-GP finally results as indicated in what follows

$$\begin{cases} \left(\frac{d(V_{tot}/m_p)}{d\Omega_s}\right)_{T,p}^{PE} = \frac{1}{\rho_p}\frac{\left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right)^0 - \left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right) + \gamma\rho_s\left(\frac{\partial^2\mu_p{}^{EoS}}{\partial\rho_s{}^2}\right)^0}{\left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right)^0 - \left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_s}\right) + \gamma\rho_s\left(\frac{\partial^2\mu_p{}^{EoS}}{\partial\rho_s{}^2}\right)^0 - \left(\frac{\partial\mu_p{}^{EoS}}{\partial\rho_p}\right)} \\ (V_{tot}/m_p)\big|_{\Omega_s=0} = \frac{1}{\rho_p{}^0} \end{cases} \tag{14}$$

It should be noted that the pseudo equilibrium partial specific volume predicted by all versions of DGRPT model described above results to be null when evaluated in the limit of infinite dilution for solute. The latter characteristic, together with positive value resulting for the same variable at finite solute concentration is indeed what inspired the empirical relations in Eq.(11) and (13), in the attempt to mimic the qualitative characteristic of experimental evidences represented in the previous section.

In what follows, both NE-RS and DGRPT methods are utilized to model gas sorption in conventional glassy polymers using the PC-SAFT EoS. For the DGRPT approach, the original formulation was selected. This choice is predicated on the primary objective of this study: rather than identifying which model yields the most accurate numerical predictions, we aim to examine the fundamental nature of the phenomenon and identify the essential theoretical foundations required to address the problem. Consequently, efforts were made to minimize empirical data fitting unrelated to pure components, with the notable exception of the binary interaction parameter. The specific role and physical significance of this parameter are discussed in detail in subsequent sections.

4. Comparison with experimental data

In this section a direct comparison for the solubility and swelling predictions of the two analysed models is presented. Until now the comparisons between the two approaches were shown only for PIM-1 [18]. On the other hand, DGRPT has been used to calculate sorption in a conventional glassy polymer in only one case [33]. To fully understand the power of this model, and have a fair comparison with NE-RS, only conventional glassy materials are considered in the present work. Indeed, only for these materials the equation of state parameters of the polymer, that are necessary for both the applications, can be independently determined by fitting equilibrium data over *Tg*. For super glassy materials instead, these parameters must be retrieved with other techniques: such as the fitting directly to lower pressure absorption data [15,32]. Moreover, only cases where a not negligible swelling is induced in the matrix are considered, since both models collapse in basic no-swelling NET-GP when solute sorbed is not sufficient to substantially change volume per polymer mass in the matrix.

In the discussion which follows the original version of DGRPT model will be considered (DGRPT v1) at first, as it can be applied through a pure predictive procedure for the case of conventional glassy polymers, just as it happens for the case of the NE-RS model.

The sorption of CO_2 in polycarbonate (PC) is examined first. For this system, the binary interaction parameter (k_{sp}), the Eos parameters and the isothermal compressibility had already been determined in a previous work [19] through the analysis of true thermodynamic equilibrium solubility data. Subsequently, the model parameter χ is evaluated as the ratio between the compressibilities of the glassy and melt polymer phases at the transition point and the corresponding estimate of the model parameter χ for PC is reported in Table 2.

The high-pressure CO_2 uptake in PC, as predicted by the (NE-RS) PC-SAFT and DGRPT models at 35 °C, is then compared with experimental measurements reported by Wissinger and Paulaitis [23]. This comparison is presented in Fig. 4. The strong agreement between the model predictions and the experimental high-pressure data demonstrates the effectiveness of both the equilibrium and non-equilibrium modelling frameworks for NE-RS model.

To highlight the importance and implications of the assumptions adopted for volume swelling within the NE-RS framework, Fig. 4 also presents model predictions obtained by neglecting sorption-induced swelling of the glassy polymer matrix. Under this simplifying hypothesis the phase equilibrium calculations are performed by assuming that the pseudo-equilibrium polymer density, ρ_{pol}^{PE}, remains equal to the dry polymer density at the same temperature, regardless of the gas pressure.

Inspection of the results shown in Fig. 4 indicates that an explicit treatment of sorption-induced volume swelling does not influence the

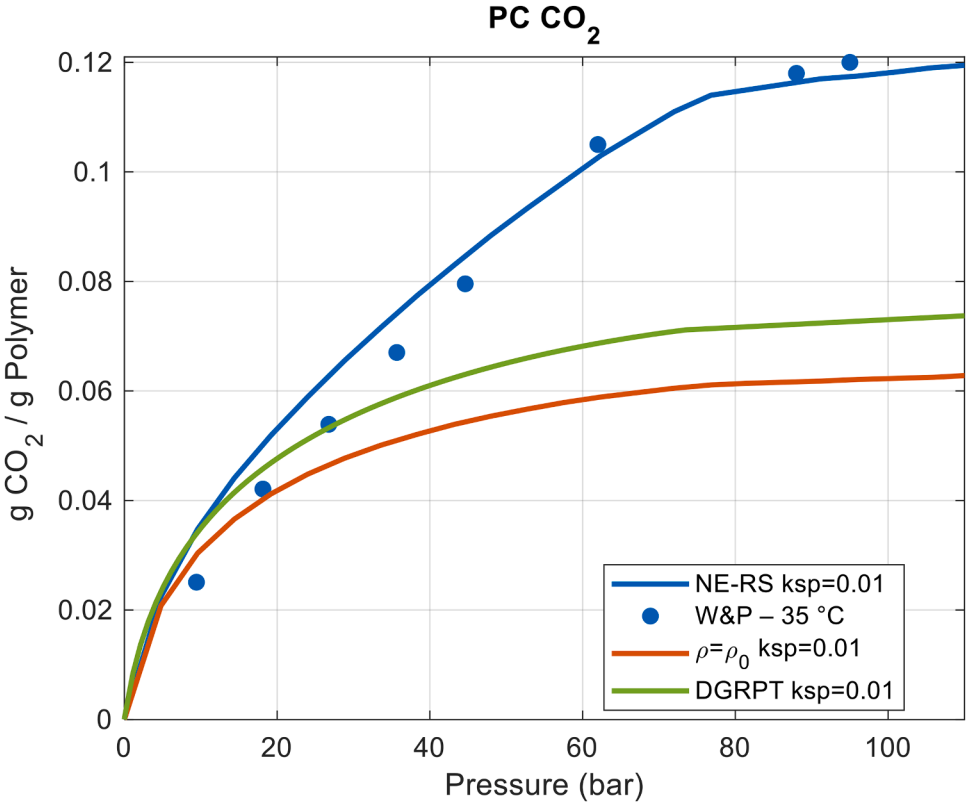

Fig. 4. NE-RS and DGRPT and constant density NET-GP model predictions (continuous lines) of CO_2 sorption in PC as function of pressure. Blue dots are experimental data from [23].

infinite-dilution solubility coefficient, in agreement with the discussion presented in a previous work [18]. Moreover, the impact of swelling on the predicted penetrant uptake in glassy PC is negligible up to a solute mass fraction of approximately 2 %. At higher concentrations, however, the role of swelling becomes significant.

These findings clearly indicate that incorporating sorption-induced volume swelling is essential for an accurate description of vapor sorption at moderate to high activities.

On the other hand, DGRPT fails to accurately predict CO_2 sorption at pressures above 20 bar. In this case as well, the infinite-dilution parameter remains unaffected by the model, since polymer dilation is negligible. The predicted sorption isotherm closely follows the non-swelling case up to approximately 18 bars, beyond which a slight deviation appears due to the onset of minor polymer dilation. This behaviour is very similar to the case reported by Marshall [33] for PMMA, another dense, conventional polymer. These results confirm that the first and simplest formulation of DGRPT struggles to describe sorption in dense polymeric materials, whereas it provides improved predictions for less dense polymers such as PTMSP [20].

To better understand the differences between DGRPT and NE-RS predictions, it is useful to analyse the effect of the solute-polymer binary interaction parameter k_{sp}. Figs. 5 and 6 report the model predictions obtained at different values of k_{sp}. In the Marshall model, the binary interaction parameter significantly influences only the low-pressure solubility S_0, while it has a negligible effect on the predicted solubility at high pressures. In contrast, within the NE-RS framework, k_{sp} affects not only S_0 but also the slope of gas uptake as pressure increases, allowing the model to accurately reproduce the experimentally observed linear growth. However, in a consistent thermodynamic framework, when the exact dry density of a polymer is known, the k_{sp} parameter should be fitted to infinite dilution solubility (S_0) rather than the high-pressure sorption range [15]. Under this approach, the swelling model is responsible for accurately reproducing high-pressure data, without any need to adjust the thermodynamic binary interaction parameter.

In Fig. 7 results are compared for volume swelling as predicted by NE-RS and DGRPT models with data directly measured by Wissinger and Paulaitis for the sorption of CO_2 in PC at 35 °C up to 100 bar. It can be observed that the good job NE-RS does in predicting the solubility isotherm is the result of a prediction of volume swelling phenomena which captures the experimental trend in the whole pressure range, while it underestimates the value by roughly 20 %. On the other side, data in Fig. 7 clarify the difficulties shown by DGRPT model predictions in representing medium and high-pressure solubility data are originate by a too poor prediction of induced volume swelling.

Similar conclusion can be drawn when the sorption of CO_2 in PMMA is analysed. This system allows for the comparison with a different conventional glassy polymer and enables evaluation of NE-RS predictions against those previously proposed by Marshall [20]. The PMMA EOS parameters were taken from[33], while k_{sp} was treated as the only adjustable parameter. The parameter χ was obtained from [19]. Experimental data, shown as blue symbols, are taken from the measurements of Wissinger and Paulaitis. As illustrated in Fig. 8, conclusions like those drawn for the previous case studies can be reached.

A further illustrative example of how crucial is representing volume swelling in the description of vapor sorption into glassy polymers is provided by the fitting of acetonitrile solubility data in PC using the (NE-RS) PC-SAFT and DGRPT models, as shown in Fig. 9. The experimental measurements, displayed as symbols, were reported by Giacinti Baschetti and co-workers [22], while the calculated isotherms, represented by continuous lines, were obtained using PC-SAFT parameters for acetonitrile taken from the literature, with the binary interaction parameter k_{sp} treated as the sole adjustable parameter. The pure-component PC-SAFT parameters adopted in the calculations and the optimized value of the binary interaction coefficient are listed in Tables 1 and 2, respectively. Results for predicted volume sweeling in PC as induced by C_2H_3N sorption are reported in Figs. 10 and 11 and compared with experimental data measured by Giacinti et al. [35]. In

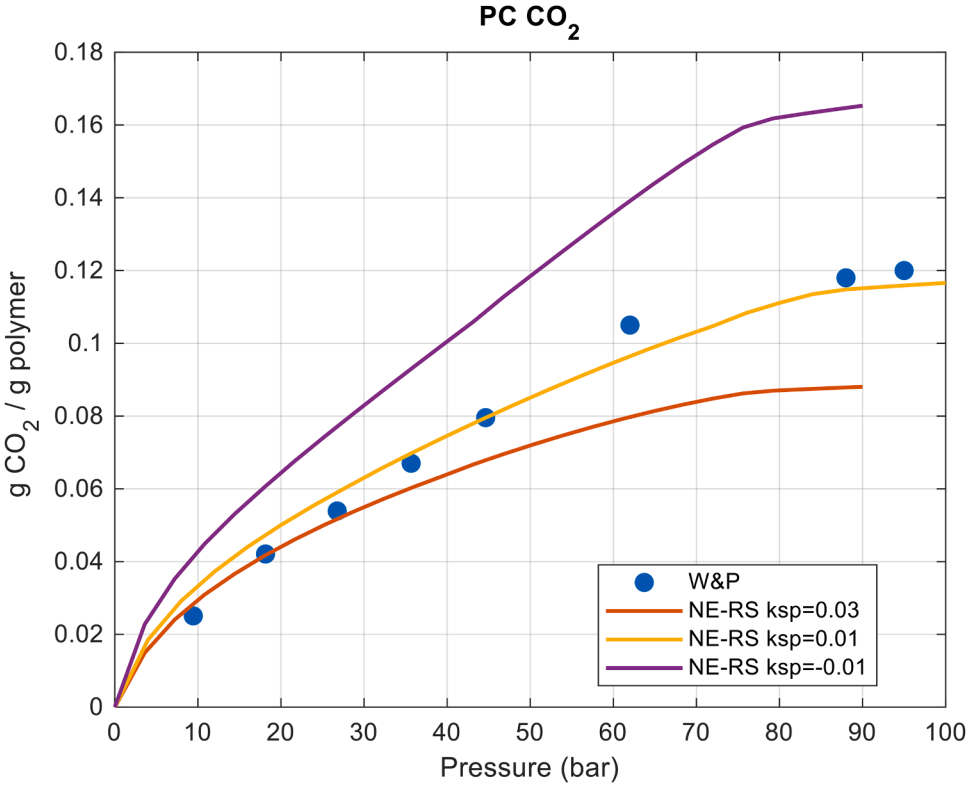

Fig. 5. NE-RS model prediction of CO_2 sorption in PC as function of pressure. Blue dots are experimental data from [23] and the 3 continuous lines are model prediction at different k_{sp}.

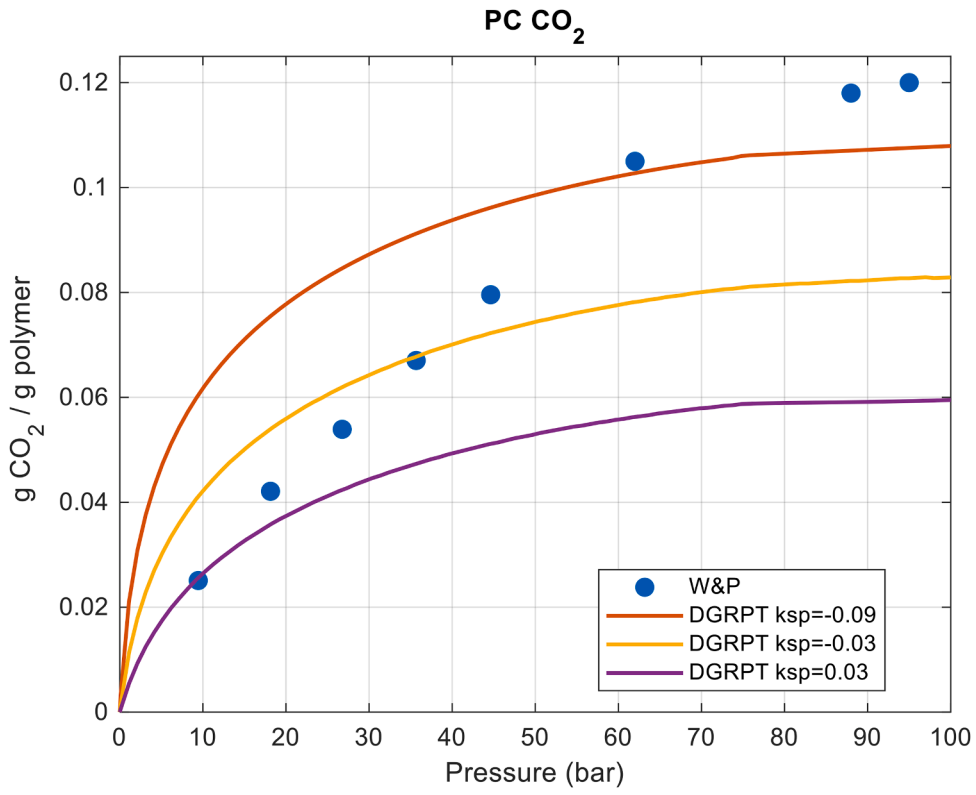

Fig. 6. DGRPT model prediction of CO_2 sorption in PC as function of pressure. Blue dots are experimental data from [23] and the 3 continuous lines are model prediction at different k_{sp}.

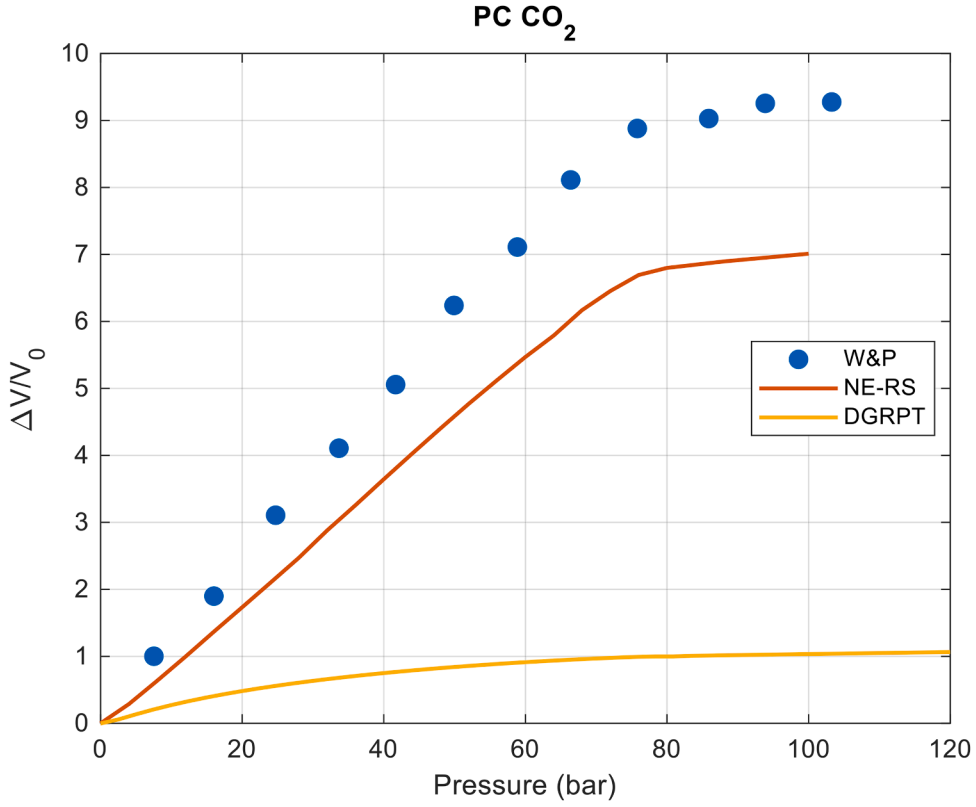

Fig. 7. PC volume dilatation at 35 °C due to CO_2 sorption at different pressures. Experimental data from [23] compared with NE-RS and DGRPT prediction.

this case, NE-RS capture the trend of volume swelling, both when considered as function of solute fugacity and as function of solute

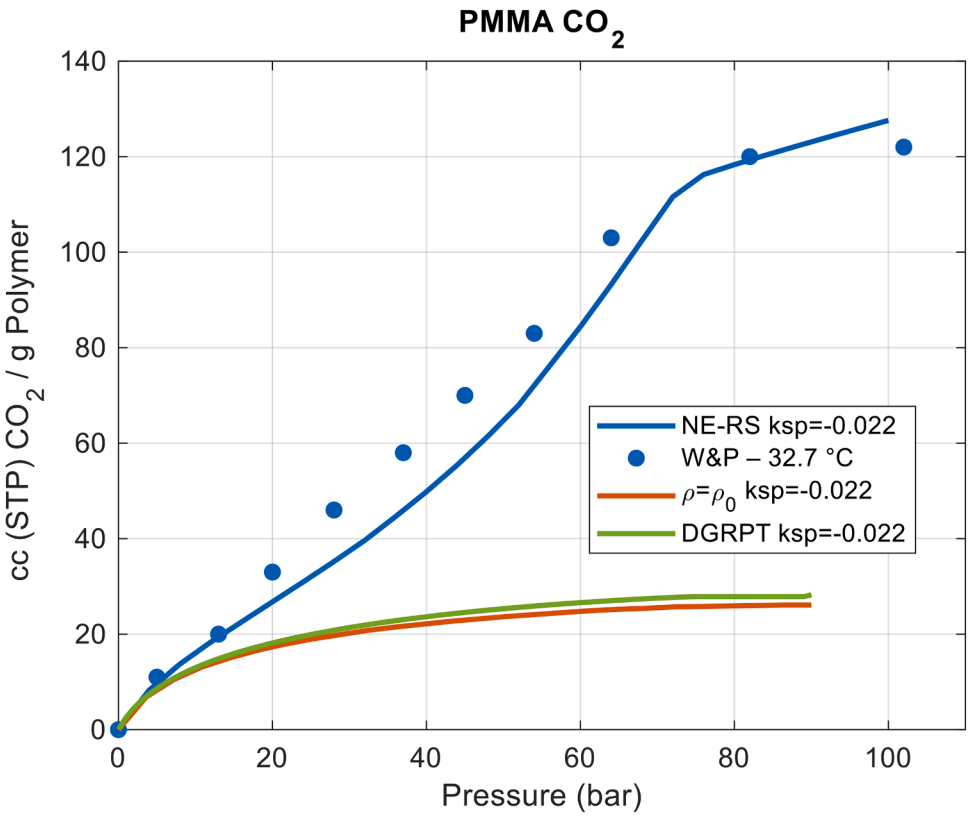

Fig. 8. PMMA CO_2 sorption as function of pressure at 32.7 °C. Experimental data from Wissinger and Paulantis et al. [23] compared with NE-RS and DGRPT.

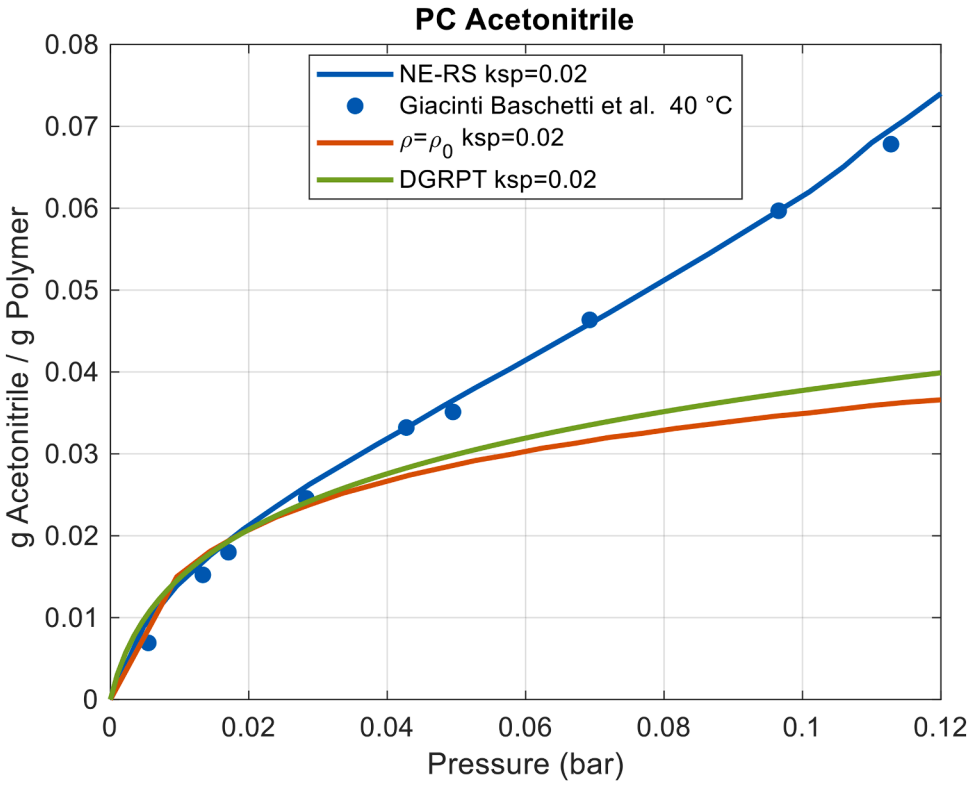

Fig. 9. DGRPT (green line) and NE-RS (blue line) model prediction of acetonitrile sorption in PC as function of pressure compared with experimental data (blue dots) from [22] and constant imposed density NET-GP (red line).

concentration, while it overestimates the value by roughly 30 %. On the other side, DGPRT prediction largely underestimates polymer swelling

Table 1
PC-SAFT parameters used in this work.

	M (g/mol)	ε/k (K)	σ (Å)	m/M	Ref
PC	∞	275.00	3.0630	0.04100	[18]
PMMA	∞	286.92	3.0210	0.04420	[33]
CO_2	44.000	169.21	2.7852	0.04711	[4]
C_2H_3N	41.050	311.31	3.1898	0.05674	[40]

Table 2
Polymers pure and binary parameters.

Ref [41]	χ	Tg (°C)	ρ_g^0 (Trif) [g/cm^3]	α_g [K^{-1}]	k_{sp} CO_2	k_{sp} C_2H_3N	k_{sp} C_2H_4
PC	0.69	150	1.194 (35 °C)	2.0×10^{-4}	0.03 (PC-SAFT)	0.02 (PC-SAFT)	/
PMMA	0.69	105	1.178 (32.7 °C)	1.7×10^{-4}	−0.22 (PC-SAFT)	/	−0.08(PC-SAFT this work) −0.0372 (DGRPT v2 PC-SAFT) −0.07 (PC-SAFT) DGRPT v1 [33]
PEMA	0.83	61	1.124 (15 °C)	2.8×10^{-4}	0.02 (SL)	/	/

and fails to capture, in qualitative terms, its trend with solute fugacity.

As mentioned in the previous section, updated versions of DGRPT model have been recently proposed to improve the capability in representing vapor induced volume dilation in glassy polymers, in which additional model parameters are considered.

Different from the case of χ parameter in NE-RS, which is both measurable from experimental data and intrinsic to the specific polymer, the λ parameter in DGRPT v2 introduced in the previous section is specific to each polymer–penetrant pair and must be fitted, with the similar concept that is applied when NET-GP is coupled with an empirical linear swelling [15,32,36]. To overcome this limitation, Baldanza et al. [37] proposed a method to determine λdirectly from the properties of the polymer–gas mixture, eliminating the need for fitting. If this approach proves successful, it could be interesting to extend it also to NE-RS model for super-glassy polymers, where the isothermal compressibility over T_g cannot be obtained from equilibrium data.

Similar considerations apply to the most recent version of DGRPT [34], indicated as DGRPT v3 in the previous section, in which the parameter $\gamma$is fitted for each polymer–penetrant pair, leading to a significantly improved capability to describe the sorption behavior of a wide range of gases and vapors in super-glassy polymers.

Example of application of both DGRPT v2 and DGRPT v3 are offered in Fig. 12, with respect to the analysis of the same set of data considered above for volume dilation of PC as induced by sorption of acetonitrile. Rather than attempting the best fit of sorption data, model results from DGRPT v2 for a limiting value of the parameter (λ =0.96), together with those from DGRPT v3 ($\gamma = -2.2$) are compared with that of original DGRPT model (DGRPT v1, corresponding the case $\lambda = 0$ and $\gamma = 0$). For the sake of comparison, in the same figure results are also reported for the case in which the partial specific volume of the solute is interpreted through the equilibrium model [see Eqs.]. It can be observed that all versions of DGRPT model returns solute partial specific volume which are negligible in the limit of infinite dilution. On the other hand, only model versions endowed with adjustable parameters allow for the representation of increase in partial specific volume in the order of equilibrium value when solute concentration increases, in accordance with experimental data.

The above results allow several general considerations to be drawn.

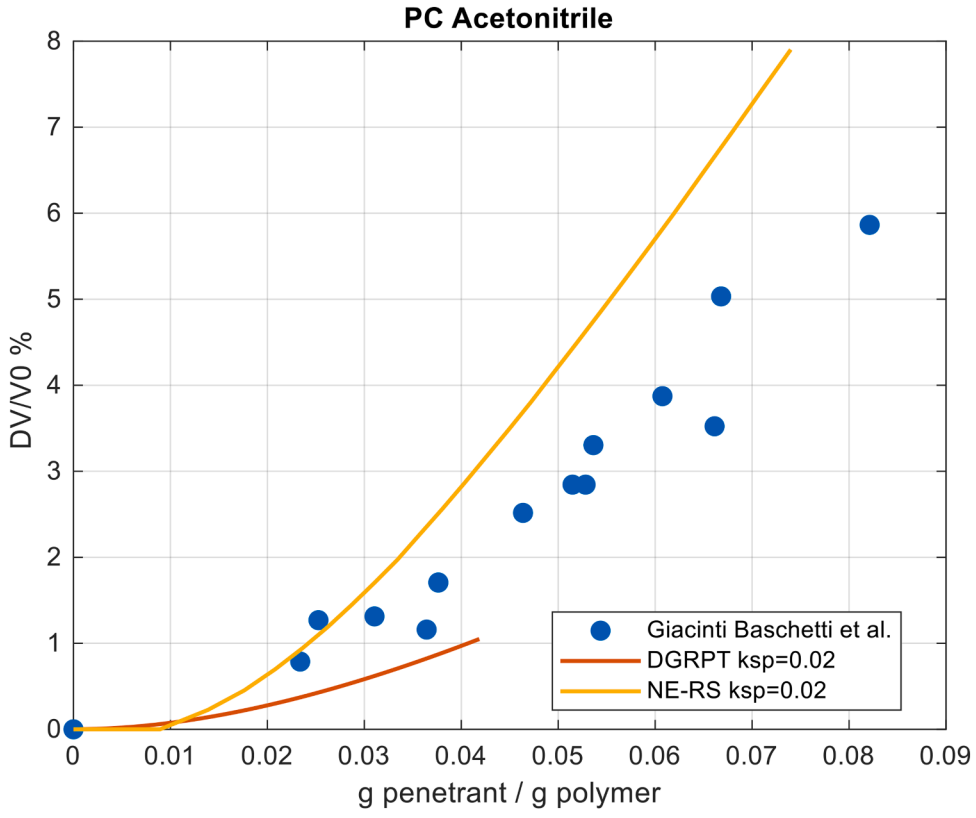

Fig. 10. PC density changes due to Acetonitrile sorption at different solute uptakes. Experimental data from [22] compared with NE-RS and DGRPT prediction at 40 °C .

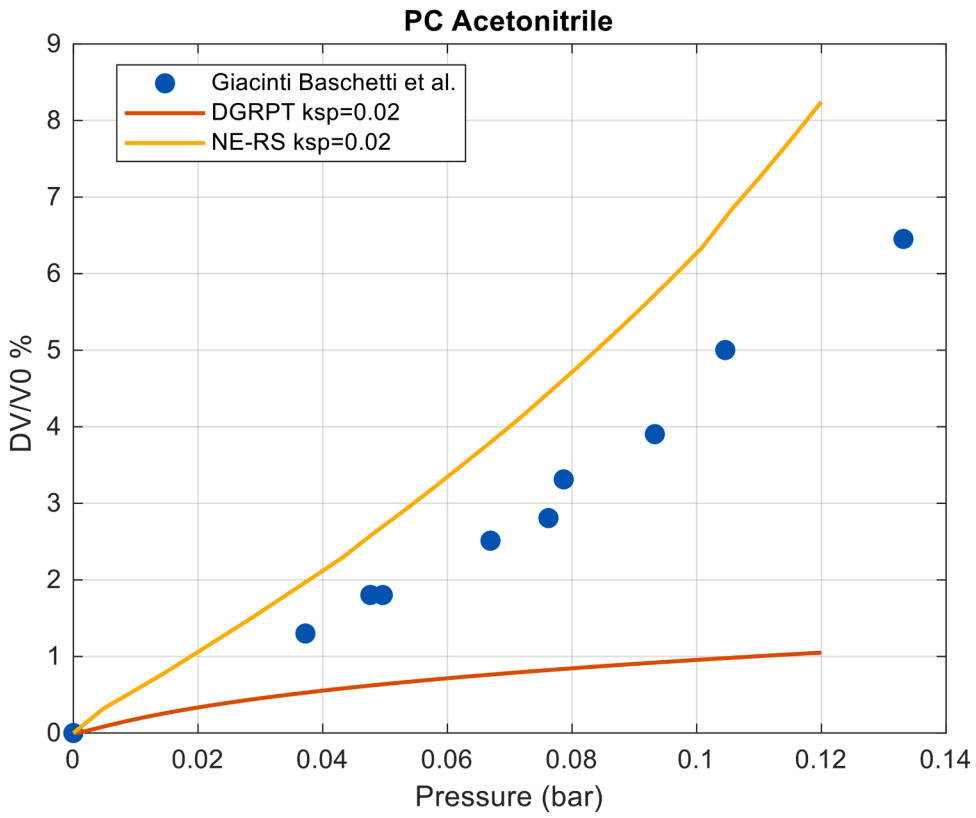

Fig. 11. PC volume increase with Acetonitrile sorption as function of pressure. Experimental data from Giacinti Baschetti et al. [22] compared with NE-RS and DGRPT prediction at 40 °C.

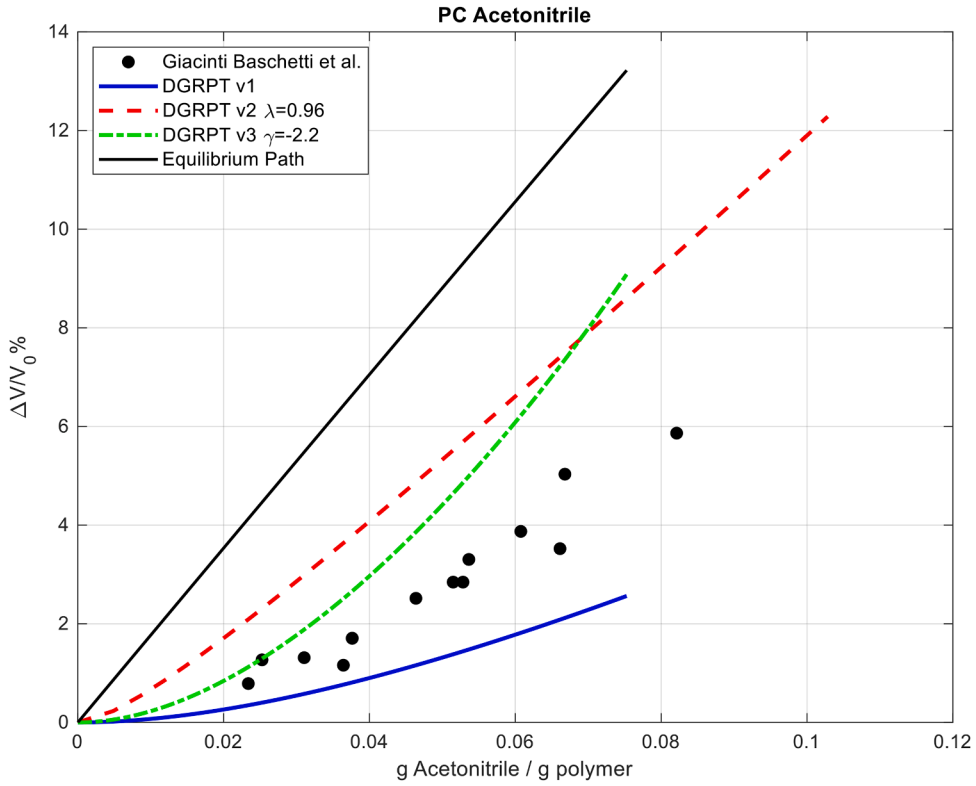

Fig. 12. PC volume changes due to Acetonitrile sorption at different solute uptakes. Experimental data from [22] compared with all DGRPT different versions and equilibrium predictions at 40 °C .

In particular, they indicated that an accurate description of sorption at high gas and vapor activities in glassy polymers requires the incorporation of glass compressibility effects within the modelling framework, either through empirical correlations or physically based formulations. Accordingly, all models rooted in the NET-GP theory require, in addition to the equation-of-state parameters of both the polymer and the penetrant and the initial density of the glass, an additional parameter that effectively accounts for the compressibility of the polymeric matrix.

In the same respect, it must be noted that only the cases of direct gas/vapor sorption in conventional glassy polymers prepared according to standard protocols have been considered in this work. While the analysis was here limited to those cases for the sake of a more significant comparison between model predictions, it must be stressed that non-equilibrium solubility in glassy systems strongly depends of specific thermal and sorption history of the sample, leading to clear hysteresis phenomena [38,39]. Indeed, hysteresis phenomena can be represented within NE-RS model, when the compressibility parameter χ is considered to be sensitive to previous sorption history, while only updated versions of the DGRPT mentioned above can be similarly used by assuming the specific model parameters are, as well, dependent on past history.

It should be finally noted that when additional specific model parameters, required to represent the complexity of solvent induced volume dilation in polymer glasses, have precise physical significance for the dry matrix, as for the case of compressibility ratio χ in NE-RS model, options are available for their evaluation through molecular dynamics approaches which have been specific tailored to address structural properties of polymeric phases below the glass transition temperature [40].

5. Conclusions

Features of sorption induced volume dilation in glassy polymers were here examined, as they result from experimental data and represented by the two distinct models proposed within the NET-GP framework.

The analysis of sorption-induced swelling in glassy polymers presented in this study underscores the critical necessity of explicitly incorporating matrix dilation into thermodynamic modelling frameworks. It should be stressed that, while infinite dilution solubility coefficient can be determined based on information about dry polymer mass density only, the accurate prediction of penetrant uptake at moderate to high activities is fundamentally dependent on the ability to model the concurrent swelling of the polymer matrix. This conclusion is robustly supported by the comparative evaluation of the Non-Equilibrium Restrained Swelling (NE-RS) model and the Dry Glass Reference Perturbation Theory (DGRPT), both rooted in the Non-Equilibrium Thermodynamics for Glassy Polymers (NET-GP) theory.

The application of the NE-RS model to conventional glassy polymers, such as Polycarbonate (PC) and Poly (methyl methacrylate) (PMMA), demonstrated solid predictive capabilities, particularly in describing the linear increase of gas uptake with pressure. The success of the NE-RS framework is attributed to its utilization of the χ parameter, a characteristic of out-of-equilibrium state of the polymer, representing the ratio of the glassy polymer's apparent compressibility to its equilibrium compressibility at the glass transition temperature. Because this parameter is intrinsic to the material and measurable from experimental pressure-volume-temperature (pVT) data, NE-RS provides a physically grounded description of the system without relying heavily on arbitrary fitting parameters for the swelling behaviour. The model's ability to reproduce high-pressure experimental data for CO_2 and acetonitrile sorption in PC confirms that accounting for the "restrained" nature of swelling in dense glasses is essential for capturing the thermodynamics of the system accurately.

On the other hand, the evaluation of the DGRPT model highlights both the theoretical innovation and the practical limitations of the perturbation approach. The original first order formulation of DGRPT, which seeks to eliminate the need for independent calculation of non-equilibrium polymer density, by trying to estimate it from the polymer chemical potential analysis, was found to struggle with dense, conventional polymers. Specifically, it tends to underestimate the swelling and consequent sorption capacity at pressures exceeding 20 bar, as evidenced by the deviations observed in the CO_2-PC and CO_2-PMMA systems. This limitation, as suggested by Marshall, stems from the truncation of the Taylor series expansion at the first order, which appears to underestimate the effect of the thermodynamic perturbation on the polymer chemical potential by the sorbent penetration at high pressures. While the updated versions of DGRPT incorporating the linear or a second-order term with additional adjustable parameters show improved accuracy, they inevitably introduce a dependence on empirical fitting specific to each polymer-penetrant pair, thereby diminishing the model's purely predictive advantage.

Ultimately, this work establishes that a robust thermodynamic model for glassy polymers must account for the compressibility of the glassy matrix, either through the structural parameters of the NE-RS model or the perturbation terms of the DGRPT. For conventional glasses where equilibrium data is available, NE-RS remains the more reliable tool, since al parameters can be estimated "objectively". However, for super-glassy polymers like PIM-1, where equilibrium states are inaccessible, this parameter holds a physical meaning, but at the moment must be fitted as well as the gamma term of the third version of DGRPT.

Eventually, the continued development of these physically based models is indispensable for advancing the design and application of polymeric materials in membrane separation and barrier technologies.

Notation

α_g: Thermal expansion coefficient of the glassy polymer
γ: Second-order interaction parameter (DGRPT v3)
λ: Adjustable parameter (DGRPT v2) to modulate the linear swelling term
ε/k: characteristic interaction energy (PC-SAFT parameter)
κ_g: glassy polymer isothermal compressibility glassy polymer
κ^{EQ}: Equilibrium isothermal compressibility of the polymer
μ_s^{NE}: Chemical potential of the solute in the non-equilibrium glassy state
μ_s^{EQ}: Chemical potential of the solute in a equilibrium state
μ_p: Chemical potential of the polymer
ρ_{pol}: Polymer mass density
ρ_{pol}^{PE}: Pseudo-equilibrium polymer density
ρ_g: Glassy polymer density
ρ_g^0: Dry glassy polymer density
ρ_s: Solute mass density / concentration
σ: hard sphere diameter (PC-SAFT model parameter)
χ: Weighting factor representing the fraction of "soft" elements (NE-RS model)
Ω_s: Solute mass ratio
f_s: Solute Fugacity
k_{sp}: Binary interaction parameter
m_p: total polymer mass
M: Molecular weight
m/M: Segment number per unit of molecular mass (PC-SAFT parameter)
p: Pressure
S_0: Infinite dilution solubility
T: Temperature
Tg: Glass Transition Temperature
Tref: Reference Temperature
V_{pol}: Total specific volume per unit polymer mass
V_{pol}^{EQ}: Specific volume of the polymer at full thermodynamic equilibrium

$\mathbf{V_g}$: Specific volume of the "hard" (frozen) relaxation elements (NE-RS model)
$\mathbf{V_{pol}^0}$: Specific volume of the dry glassy polymer at low pressure
$\overline{V}_S$: Partial specific volume of solute component
$\mathbf{V_{tot}}$: Total volume in polymer-solute system

CRediT authorship contribution statement

Ferruccio Doghieri: Writing – review & editing, Conceptualization. **Roberto Parchi:** Writing – original draft, Investigation. **Giulio Cesare Sarti:** Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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