Fluid Phase Equilibria 595 (2025) 114410

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.sciencedirect.com/journal/fluid-phase-equilibria

A second-order Dry Glass Reference Perturbation Theory for modeling sorption in glassy polymers: applications to systems containing light gases, alcohols, and water vapor

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ARTICLE INFO

Keywords:
Polymer membranes
Gas and vapor sorption
Equations of state
PC-SAFT
Non-equilibrium thermodynamics for glassy polymers

ABSTRACT

The solubility of gases and vapors plays a critical role in determining the overall performance of membrane-based separation processes. Through the use of advanced Equations of State (EoS), the Non-Equilibrium Thermodynamics for Glassy Polymers (NET-GP) theory rose into prominence as a powerful correlative and predictive tool for the sorption of guest species in glassy polymers. The recently proposed Dry Glass Reference Perturbation Theory (DGRPT) provided a method to account for the polymer swelling through the NET-GP framework. In this work, we introduce a second-order modification to the DGRPT that improves upon the model's flexibility in representing different types of isotherms. We have also investigated different association and parameterization schemes for water and alcohol sorption using the PC-SAFT EoS in glassy polymers. For the non-self associating polymers investigated here, our results concluded that the sorption of alcohols can be represented adequately using the induced association assumptions formulated by Kleiner and Sadowski. On the contrary, the same assumptions often lead to poor water sorption results. We speculate that the Wolbach and Sandler combining rule may be incapable of representing the cross-association effects between water and the glassy polymer. As a result, we fitted the cross association volume of bonding ($\kappa_{A_iB_j}$) on the sorption data while fixing the cross association energetic parameter ($\epsilon_{A_iB_j}$) to half of water's parameter. The adjusted $\kappa_{A_iB_j}$ can then be treated as a temperature-independent parameter, while the effects of temperature variation can be delegated to the binary interaction parameter (k_{ij}).

1. Introduction

In recent years, the growing interest in membrane-based separation processes has been primarily facilitated by its low energy consumption, cost effectiveness, and ease of maintenance and operation compared to the incumbent thermal separation processes (i.e., distillation, absorption, etc) [1,2]. In particular, polymers as a class of materials have been an attractive choice for membranes due to their ubiquity, processability, and affordability [3,4]. Hence, a deep understanding of what governs the performance of such systems is essential in the development of novel materials and processes involving polymer membranes.

The solution-diffusion model is the most widely accepted theory in explaining the transport of gases, vapors, and liquids in dense polymeric membranes [5]. The theory postulates that the permeability of a guest species can be described as the product of the solubility and the diffusivity. Hence, the solubility of a penetrant can provide useful information on the membrane application in question. For example, in processes involving CO_2/light gases mixtures separation, the solubility of CO_2 is higher than that of the other species [6,7]. In situations like this, the solubility-selectivity is crucial in the determination of the overall selectivity. Thus, a judicious polymer membrane selection for CO_2 separation will favor a high CO_2 solubility-selectivity. Moreover, in recent modeling work involving the separation of complex organic liquids [8–10], it was shown that when the process is mainly driven by solubility, direct prediction of the permeate composition can be achieved based on the penetrant solubilities alone and without prior knowledge of the diffusivities.

In both of the formerly mentioned cases, accurate solubility models would be essential in determining the separation performance across various operating conditions. In the current literature, the dual mode sorption (DMS) model [11–17], the Guggenheim, Anderson, and de Boer (GAB) model [16,18–23], and the non-equilibrium thermodynam-

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https://doi.org/10.1016/j.fluid.2025.114410
Received 13 December 2024; Received in revised form 20 February 2025; Accepted 2 March 2025
Available online 11 March 2025

ics for glassy polymers theory (NET-GP) [24–28] are the most popular models that are used for such purposes.

The DMS model assumes that the penetrant molecular population is divided into two separate groups. The first dissolves into the bulk of the polymer and is governed by Henry's law, and the second fills in the microvoids of the membrane and obeys Langmuir's adsorption isotherm. With three adjustable parameters, the DMS model can correlate the sorption isotherms of most penetrants remarkably well. Sigmoidal shaped isotherms, such as alcohol sorption isotherms in PTMSP [29,30], are among the few cases where the model fails to fit the curve appropriately [31]. The DMS model can also be extended to predict the sorption behaviors of gas and vapor mixtures, however, owing to the empirical nature of the model, several parameterization issues may arise. In a sensitivity analysis study conducted by Ricci et al. [32], the authors have shown for the case of CO_2/CH_4 mixtures, different DMS parameters, resulting in similar quality of fit to the pure sorption data, can lead to vastly different mixed gas predictions.

The underlying physical mechanism governing the GAB model [18–20] is multi-layer adsorption. Motivated by the high free volume and the microvoids present in families of polymers like PIMs [23], the GAB model had found some appeal as an alternative to the more popular DMS model. Under high pressures and activities, the high uptake of the vapor can lead to a glass transition, and the polymer enters the rubbery regime. This is characterized by a change in concavity of the sorption isotherm and an upturn as the polymer departs from the glassy state. Interestingly, the GAB model was found to be flexible enough to correlate the entirety of the sorption isotherm before and after the sorption-induced glass transition. As such, it was successful at correlating the solubility isotherms of both high free volume polymers (i.e PIM-1 [23], PIM-EA-TB [21] and PTMSP [22]), and rubbery polymers (i.e. PDMS [33]). However, a major downside to the model is the difficulty of extending it to mixture cases. Current attempts in literature [34] involve introducing additional penetrant–penetrant interaction parameters, which require fitting to the available mixture data, hence, limiting the predictive capabilities of the model.

Another approach of modeling gas sorption in glassy polymers relies on the NET-GP framework [24,25]. By extending equilibrium Equations of State (EoS) to their non-equilibrium form (i.e. NE-EoS), the pseudo-equilibrium state at which the external gas/vapor and the glassy phases exist in can be described, leading to the determination of the sorbent composition in the polymer. For nearly three decades since the development of the NET-GP theory, the Sanchez and Lacombe Lattice Fluid (LF) [24–28,35–39], the Perturbed Hard-Sphere-Chain (PHSC) [28,40,41], the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) [42–45], and the Non-Random Hydrogen Bonding (NRHB) [46–50] equations of state, among many others, were used for sorption calculations. The performance of the NET-GP approach inherits the predictive capabilities of the EoS of choice. For instance, the NELF model can provide good predictions of the sorption behavior for mixed gases [51–53] and in polymer blends [31,54]. In addition, NE-SAFT-type EoS can be extended to describe the sorption behaviors of copolymers from the homopolymer data [55–58]. To our knowledge, NE-SAFT-type EoS have not been applied yet in modeling the gas sorption in glassy copolymers and it will be investigated in our subsequent work.

However, the NE-EoS also inherit the flaws and limitations of their equilibrium versions. In particular, issues plaguing the estimation of the pure polymer parameters for phase equilibria calculations are prevalent, and applications related to sorption in glassy polymers are no exception. Moreover, most high performing polymers (i.e. PIMs and polyimides) exhibit very high glass transition temperatures (T_g), hence, pure pressure–volume–temperature (PVT) data, which are conventionally used for the parameterization procedure, are seldom available. As a result, practitioners in the field often regress these parameters to sorption data alone [10,26,27,39,59–62], which requires access to multiple gas/vapor species isotherms to find a set of transferable parameters.

In its formulation, the NET-GP theory also requires the dry polymer's density as an input in order to carry out the calculations. In certain cases, especially at higher pressures and activities, the polymer matrix can swell. To account for this, a linear, *ad hoc* swelling model is typically used, thereby introducing the swelling coefficient as an additional adjustable parameter. In an attempt to predict the polymer's dilation without relying on the *ad hoc* model, Minelli and Doghieri [63–65] augmented the NET-GP with a rheological model, relating the equilibrium specific volume of the rubbery phase to the glassy phase. This modification of the theory requires the estimation of an additional, solute-independent, pseudo-equilibrium parameter, which can be determined from the polymer's volumetric data.

More recently, Marshall et al. [61] proposed a modified NET-GP, referred to as the Dry Glass Reference Perturbation Theory (DGRPT), that allows the NE-EoS to determine the solubilities of the penetrants and the dilation of the polymer simultaneously. In the many works that followed, the DGRPT and the simplified [66] Polar [67] PC-SAFT (or sPPC-SAFT) EoS were applied successfully in modeling the sorption of vapors and complex organic liquids in glassy membranes [9,10,62,68].

In this paper, we choose the DGRPT to model light gas and vapor sorption in glassy polymers. As we have alluded to earlier, the strength of the NET-GP theory (and by proxy, the DGRPT) comes from the appropriate choice of the EoS. The PC-SAFT EoS has been proven to be versatile in modeling a variety of thermodynamically challenging systems [69], and will be our chosen EoS. However, there are some accuracy issues related to the description of the dilation of the polymer matrix that should be addressed by modifying the DGRPT. In addition, appropriate parameterization strategies related to the PC-SAFT, particularly for cross-association interactions, are yet to be investigated systematically in sorption cases involving glassy polymers (see Fig. 1 for a cartoon representation of the models). Therefore, our objective here is twofold:

- In some sorption isotherms, a "Langmuirian-like" behavior can be first observed, followed by a linear relationship between the sorbent uptake and the activity (i.e. a dual-mode sorption-type isotherm). The original version of the DGRPT loses accuracy in the linear region of the isotherm. Previous attempts by Marshall [70] managed to resolve this issue; however, solving the systems of equations often leads to a dual solution. To ameliorate this, we modify the theory and introduce a higher-order version of the DGRPT.
- Associating sorbents can exhibit a variety of isotherm types. For example, alcohol sorption in polymers such as PTMSP and PTMSN [60] is sigmoidal in shape. Other alcohol-polymer systems display the typical concave sorption behaviors usually observed in non-associating penetrants, which may be followed by an upturn as the glassy polymer transitions to the rubbery state (i.e. inverse S shape).Water sorption isotherms are often convex, perhaps due to its tendency to form clusters in the polymer. In each of these cases, the cross association parameters should be addressed in different ways for an accurate representation of the isotherm, which will be explored here.

In this paper, we will start with briefly describing the NET-GP theory (Section 2.1), introduce the original DGRPT (Section 2.2), and provide a detailed derivation of the modified second-order DGRPT (Section 2.3). The sections that will follow will showcase the improved fitting capabilities of this modified model in representing "dual-mode"-like sorption (Section 3.2). Finally, the latter half of the paper will explore different association and parameterization schemes in systems containing associating vapors (Sections 3.3 and 3.4), with the ultimate goal of reducing the number of adjustable parameters and without sacrificing the quality of fit to the isotherms.

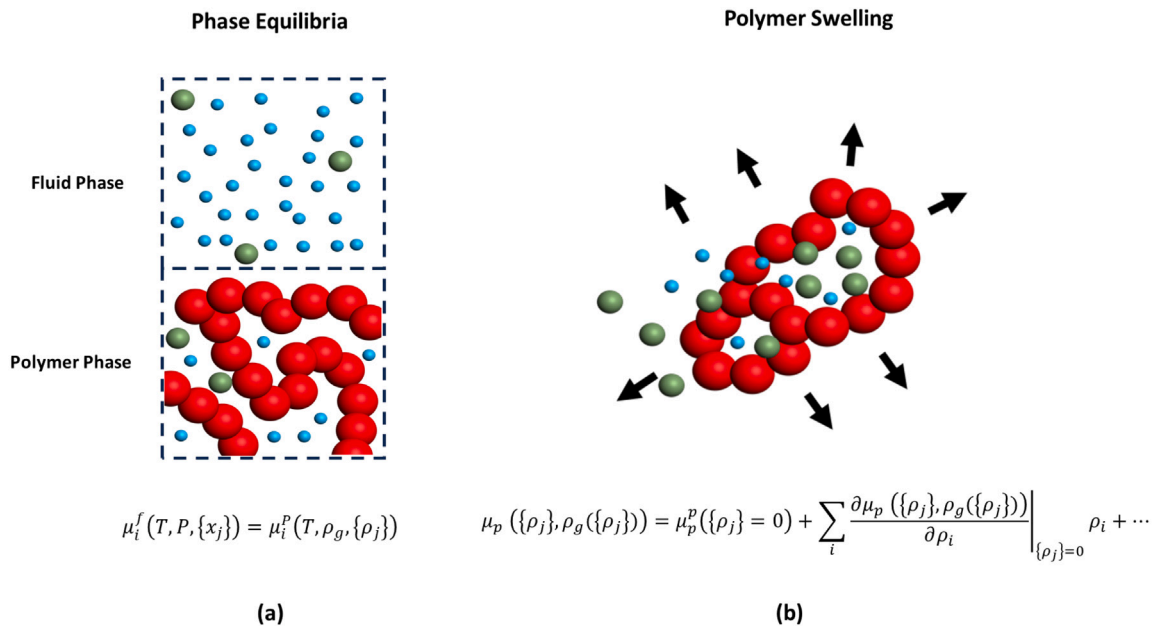


Fig. 1. A cartoon representation of the DGRPT theory. (a) The PC-SAFT equation of state provides an expression for the sorbate's chemical potential, allowing for the determination of the sorbed content in the polymer (b) By utilizing a truncated expression of the expanded polymer's chemical potential, the swollen glassy polymer density can be determined, and a closure to the Non-Equilibrium Thermodynamics For Glassy Polymer (NET-GP) theory is achieved.

2. Theory

2.1. The Non-Equilibrium Thermodynamics for Glassy Polymers (NET-GP) theory

The thermodynamics governing the solubility of guest species in rubbery polymers is well understood. At a given temperature (T), pressure (P) and composition $\{x_j\}$ of the external fluid phase containing n components, Eqs. (1) and (2) dictate the phase equilibrium conditions as follows :

$$\mu_i^f\left(T,P,\{x_j\}\right) = \mu_i^p\left(T,\rho_{pol},\{\rho_j\}\right) \quad i,j = 1,\ldots,n \tag{1}$$

$$P = P^{EoS}\left(T,\rho_{pol},\{\rho_j\}\right) \tag{2}$$

where the superscripts f and p indicate the fluid and the polymer phases respectively, μ_i is the chemical potential of component i and P^{EoS} is the EoS expression for pressure. By coupling these equations representing phase equilibrium and the EoS for the polymer mixture, respectively, the polymer number density (ρ_{pol}) and the set of number densities of the penetrants $\{\rho_j\}$ can be determined (note that the polymer is only present in the polymer phase, and its composition is not an element of $\{x_j\}$). However, in glassy polymers, the limited mobility of the polymer chains results in a density that does not reflect the equilibrium value that corresponds to the system's minimum Gibbs free energy. To address this issue, Doghieri and Sarti [24] developed the NET-GP theory to provide the formalism required to describe this pseudo-equilibrium state. By relying on the experimentally measured glassy polymer density (ρ_g) as an order parameter, the effects of departure from equilibrium can be incorporated into any thermodynamic potential, such as the reduced Helmholtz free energy ($\tilde{a}$) [71] (i.e. $\rho_{pol} = \rho_g$). Nevertheless, in systems where a sorption-induced swelling occurs, experimental values of ρ_g across the entire pressure range are seldom available and several *adhoc* models were proposed to account for this effect [51,72]. Alternatively, one can utilize Marshall et al.'s Dry Glass Reference Perturbation Theory (DGRPT) [61], which determines the polymer swelling through the NE-EoS. The next sections will provide the theoretical background on the DGRPT, followed by how a second order correction to its terms would deal with some of its previous shortcomings.

2.2. The Dry Glass Reference Perturbation Theory (DGRPT)

The derivation of the DGRPT starts with the following generalization of the relationship between the glassy polymer's density (ρ_g) and its dry density (ρ_g^0) in a fluid-glassy polymer system [61]:

$$\rho_g = \rho_g^0 \exp\frac{f\left(\rho_g,\{\rho_j\},T\right)}{kT} \tag{3}$$

where f is an unknown function of the temperature, the polymer density, the guest species densities and k is Boltzmann's constant. In certain cases, relating the polymer swelling to the amount of sorbed content instead of the pressure (or the fugacity) is more representative of the effects of swelling, such as when liquid sorbents are involved. In the original publication, Marshall et al. [61] showed that Eq. (3) can be approximated by a first-order expansion of the polymer's chemical potential (μ_p) around infinite dilution and at temperature T (note that the temperature was removed from the list of variables in the equation as it was treated as a constant during the expansion):

$$\mu_p\left(\{\rho_j\},\rho_g(\{\rho_j\})\right) \approx \mu_p\left(\rho_g^0,\{\rho_j\}=0\right) + \sum_i^n \frac{\partial \mu_p}{\partial \rho_i}\Big|_{\rho_g^0,\{\rho_j\}=0} \rho_i \tag{4}$$

This analytical expression was derived under the assumption that the density derivative approaches zero at infinite dilution, as observed by Durd'áková et al. [73]:

$$\frac{\partial \rho_g}{\partial \rho_i}\Big|_{\{\rho_j\}=0} \approx 0 \tag{5}$$

With expression (4), alongside Eq. (1), a closure to the NET-GP framework is achieved. Using an equilibrium EoS, an analytical form of the chemical potentials and their derivatives can be obtained, and the sorption of the guest species and the swelling of the polymer can be determined. However, in its current form, the DGRPT struggles to correlate some sorption isotherms with a linear dependence on the external fluid pressure. To ameliorate this issue, we propose a modified DGRPT that relies on the second order expansion of the polymer's chemical potential, which will be discussed in the next Section 2.3.

2.3. The second-order form of The Dry Glass Reference Perturbation Theory

A formal expansion of the polymer's chemical potential is given as follows:

$$\mu_p\left(\{\rho_j\},\rho_g(\{\rho_j\})\right)=\mu_p\left(\rho_g^0,\{\rho_j\}=0\right)+\sum_i^n\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\{\rho_j\}=0}\rho_i+\frac{1}{2}\sum_i^n\sum_k^n\left.\frac{\partial^2\mu_p}{\partial\rho_i\partial\rho_k}\right|_{\{\rho_j\}=0}\rho_i\rho_k+\cdots \tag{6}$$

The derivatives in Eq. (6) do not hold the glassy density constant. In other words these derivatives treat $\{\rho_j\}$ as the variables and ρ_g as a function of these quantities. Applying chain rule will result in the following expression for the first-order derivatives:

$$\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\rho_{j\neq i}}=\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\rho_g,\rho_{j\neq i}}+\left.\frac{\partial\mu_p}{\partial\rho_g}\right|_{\{\rho_j\}}\left.\frac{\partial\rho_g}{\partial\rho_i}\right|_{\rho_{j\neq i}} \tag{7}$$

Notice that the partial derivative of μ_p with respect to ρ_i on the right-hand side of Eq. (7) treats $\{\rho_j\}$ and ρ_g as independent variables i.e. $(\partial\mu_p/\partial\rho_i)_{\rho_{j\neq i}}\neq(\partial\mu_p/\partial\rho_i)_{\rho_g,\rho_{j\neq i}}$. At infinite dilution, the following notation will be adopted:

$$\lim_{\{\rho_j\}\to0}\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\rho_{j\neq i}}=\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\{\rho_j\}=0} \tag{8}$$

$$\lim_{\{\rho_j\}\to0}\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\rho_g,\rho_{j\neq i}}=\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\rho_g^0,\{\rho_j\}=0} \tag{9}$$

Hence, if the derivative treats ρ_g as a function of $\{\rho_j\}$, its limit at infinite dilution is given by Eq. (8), where it is evaluated at $\{\rho_j\}=0$, and when it treats them as independent variables, the limit is given by Eq. (9), where it will be evaluated at both ρ_g^0 and $\{\rho_j\}=0$. This notation will be applied to all the partial derivatives shown in this work. As we have explained in Section 2.2, the glassy density derivative at infinite dilution in Eq. (7) can be assumed to be zero (see Eq. (5)). The second-order derivatives of μ_p, on the other hand, also require the second-order glassy polymer density derivatives evaluated at infinite dilution (see the supplementary material A for the full expression). In this work, we assume that these glassy density second order derivatives are system-specific and must be evaluated by fitting to the sorption isotherm. Additionally,for fitting convenience, we also introduce 'second-order' parameters (γ) and link the second-order density derivatives to the chemical potential derivatives as follows:

$$\left.\frac{\partial^2\rho_g}{\partial\rho_k\partial\rho_i}\right|_{\{\rho_j\}=0}=-\left(1-\gamma_{ik}\right)\frac{\left.\frac{\partial^2\mu_p}{\partial\rho_k\partial\rho_i}\right|_{\rho_g^0,\{\rho_j\}=0}}{\left.\frac{\partial\mu_p}{\partial\rho_g}\right|_{\rho_g^0,\{\rho_j\}=0}} \tag{10}$$

Thus, using the assumptions made about the glassy polymer density derivatives at infinite dilution (i.e. Eqs. (5) and (10)), the two types of the first and second order partial derivatives of μ_p can be linked together as follows:

$$\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\{\rho_j\}=0}=\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\rho_g^0,\{\rho_j\}=0} \tag{11}$$

$$\left.\frac{\partial^2\mu_p}{\partial\rho_k\partial\rho_i}\right|_{\{\rho_j\}=0}=\gamma_{ik}\left.\frac{\partial^2\mu_p}{\partial\rho_k\partial\rho_i}\right|_{\rho_g^0,\{\rho_j\}=0} \tag{12}$$

Finally, by truncating the expansion in Eq. (6) at the second order,a quadratic approximation of the polymer's chemical potential around the dry polymer's density is obtained:

$$\mu_p\left(\{\rho_j\},\rho_g(\{\rho_j\})\right)\approx\mu_p\left(\rho_g^0,\{\rho_j\}=0\right)+\sum_i^n\left.\frac{\partial\mu_p}{\partial\rho_i}\right|_{\rho_g^0,\{\rho_j\}=0}\rho_i+\frac{1}{2}\sum_i^n\sum_k^n\gamma_{ik}\left.\frac{\partial^2\mu_p}{\partial\rho_i\partial\rho_k}\right|_{\rho_g^0,\{\rho_j\}=0}\rho_i\rho_k \tag{13}$$

From Eqs. (10) and (12), one can infer the physical implications of varying the γ parameters. Firstly, these parameters control the direction and the magnitude of the second order correction. For example, if $(\partial^2\mu_p/\partial\rho_i^2)_{\rho_g^0,\{\rho_j\}=0}$ is positive (which is the case for all of the systems investigated here), a negative γ_{ii} will decrease $(\partial^2\mu_p/\partial\rho_i^2)_{\{\rho_j\}=0}$, leading to a decrease in the polymer's chemical potential. This implicitly suggests the decrease in the polymer's composition, and hence, an increase in the sorbent uptake. Secondly, these parameters are coupled with the second-order sorbent densities terms (i.e. ρ_i^2 and $\rho_i\rho_k$). Thus, most of the sorption and swelling corrections occur at the higher pressures/activities ranges of the isotherm. Thirdly, a zero value of the γ parameters nullifies the second-order correction to the chemical potential, and reverts the DGRPT back to its linear, first-order form.

The second-order parameters γ_{ii} can be fitted to the pure sorption isotherm of penetrant i in the polymer. In principle, these parameters are transferable to the mixture cases as we will show in our upcoming work related to mixed gas sorption and copolymers. The effects of the cross second-order parameter γ_{ik}, on the other hand, at least for the cases investigated, was found to be negligible, thus it was set to null. In this work, the showcased results will be limited to pure sorption isotherms. A detailed derivation of Eq. (13) is given in section A of the supplementary material.

2.4. The Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT)

At the core of the NET-GP and the DGRPT frameworks is the equilibrium EoS. In this work, the PC-SAFT EoS [42] will be used. In this EoS, the contribution to the reduced residual free energy ($\tilde{a}^{res}$) can be split into three types of intermolecular effects:

$$\tilde{a}^{res}=\tilde{a}^{hc}+\tilde{a}^{disp}+\tilde{a}^{assoc} \tag{14}$$

The hard-chain term ($\tilde{a}^{hc}$) (i.e. the repulsive term) is the contribution from the reference chain-fluid derived by Chapman et al. [74,75], and is based on Wertheim's thermodynamic perturbation theory [76–79]. The dispersive attractions ($\tilde{a}^{disp}$) term of the chain molecules, on the other hand, was developed by Gross and Sadowski [42] as a perturbative correction to the reference chain-fluid based on Baker and Henderson's perturbation theory [80] and a isotropic square-well potential. Finally, the hydrogen bonding term ($\tilde{a}^{assoc}$) is determined using the typical SAFT form introduced by Chapman et al. [75], however, the notational convention used by Marshall [81] will be adopted here:

$$\tilde{a}^{assoc}=\sum_i x_i\left[n_d^{(i)}\left(\ln X_A^{(i)}-\frac{X_A^{(i)}}{2}+\frac{1}{2}\right)+n_a^{(i)}\left(\ln Y_B^{(i)}-\frac{Y_B^{(i)}}{2}+\frac{1}{2}\right)\right] \tag{15}$$

where x_i is the molar fraction, $n_d^{(i)}$ is the number of hydrogen donor sites, $n_a^{(i)}$ is the number of hydrogen acceptor sites, $X_A^{(i)}$ is the fraction of the unbonded donor sites, and $Y_B^{(i)}$ is the fraction of the unbonded acceptor sites for component i. The expressions for the other free energy terms are given in detail in the original PC-SAFT publication [42],and the numerical procedure to determine the site fractions is explained in section C of the supplementary material. To carry out the sorption calculations, one must acquire the pure parameters of each component involved in the system. For non-associating compounds, the m parameter represents the number of tangentially bonded spherical segments in a molecular chain, with each of these segments diameter being defined by the σ parameter. The dispersive attractions are described by the parameter ϵ, which also represents the depth of the square-well pair-potential. In the presences of hydrogen bonding, two additional parameters, the energetic association parameter ϵ_{AB}, and the volume of the hydrogen bonding κ_{AB} are required. When dealing with mixtures, appropriate combining rules must be applied. For the PC-SAFT EoS, the

Table 1
The list of the pure PC-SAFT parameters, the number of hydrogen donor and acceptor sites of the sorbents investigated in this work.

Compound	m	σ (Å)	ϵ/k (K)	ϵ_{ab}/k (K)	κ_{ab}	n_d	n_a	Ref.
Nitrogen	1.205	3.313	90.960	–	–	–	–	[42]
Methane	1.000	3.704	150.030	–	–	–	–	[42]
Carbon dioxide	2.073	2.785	169.210	–	–	–	–	[42]
Ethane	1.607	3.521	191.420	–	–	–	–	[42]
Propane	2.002	3.618	208.110	–	–	–	–	[42]
n-Butane	2.332	3.709	222.88	–	–	–	–	[42]
Methanol	1.526	3.230	188.900	2899.500	0.03518	1	1	[83]
Ethanol	2.383	3.177	198.240	2653.400	0.03238	1	1	[83]
1-propanol	3.000	3.252	233.400	2276.800	0.01527	1	1	[83]
Water	1.205	σ_w (T)[a]	353.945	2425.670	0.04509	1	1	[84]

[a] σ_w (T) = 2.7927 + 10.11 × exp (0.01775 T/K) − 1.417 × exp (0.01146 T/K).

segment size (σ_{ij}) and the cross energetic (ϵ_{ij}) parameters for a pair of components (i.e. i and j) can be determined via the Berthelot–Lorentz combining rule:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{16}$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}(1 - k_{ij}) \tag{17}$$

By default, the binary interaction parameter (k_{ij}) is set to zero. However, under most circumstances, a minor adjustment to k_{ij} may be required to correlate the sorption isotherm appropriately. For the associating parameters, the Wolbach and Sandler combining rule [82] is often used to estimate the cross-association hydrogen bonding energy ($\epsilon_{A_iB_j}$) parameter and the volume of bonding ($\kappa_{A_iB_j}$):

$$\epsilon_{A_iB_j} = \frac{1}{2}(\epsilon_{A_iB_i} + \epsilon_{A_jB_j}) \tag{18}$$

$$\kappa_{A_iB_j} = \sqrt{\kappa_{A_iB_i}\kappa_{A_jB_j}}\left(\frac{\sqrt{\sigma_{ii}\sigma_{jj}}}{\frac{1}{2}(\sigma_{ii}+\sigma_{jj})}\right)^3 \tag{19}$$

For low molecular weight compounds, like gases and vapors, the pure component parameters are often regressed to pure saturated liquid density and vapor pressure data [42,83,84]. The list of guest gas/vapor species investigated here and their parameters are reported in Table 1.

2.5. The estimation of the pure polymer parameters for the PC-SAFT equation of state

The prevailing wisdom in other branches of the phase equilibria literature suggests the usage of both pure and mixture data for the regression of the pure polymer PC-SAFT (or any equation of state) parameters [85]. On the contrary, the common consensus in the literature investigating gas and vapor sorption in glassy polymers is to fit the pure polymer parameters only to rubbery/melt PVT data. The latter approach generally does not lead to inadequate parameters, and it was successfully demonstrated on the NELF model [24,38], the NE-SAFT [28], the NE-PC-SAFT [43], and the NE-NRHB model [49] to name a few. However, for many high T_g glassy polymers, rubbery PVT data are seldom available. In cases like these, the only available data is the gas/vapor solubilities in the polymer. One way of dealing with this issue is to regress the parameters to the solubility coefficient at infinite dilution (S_0) data. By following some general heuristics, a fixed value for the binary interaction parameters (k_{ij}) between the sorbent and the polymer can be set. For example, light gases and n-alkane vapors are assumed to have a k_{ij} value of zero between themselves and the polymer (note that there may be some exceptions to this rule,such as in cases where H_2 is involved), thus, the only parameters to estimate in this optimization problem are the pure component parameters of the polymer. This approach has been applied successfully for the NELF model for many high performing polymers, which includes PIMs and polyimides [26,27,39,60]. We attempted to replicate this success with the NE-PC-SAFT by deriving an analytical form for S_0:

$$\ln S_0 = 1 + \left.\frac{\partial \tilde{a}^{(p),res}(\rho, T, x_i, x_p)}{\partial x_p}\right|_{x_i=0,x_p=1} - \left.\frac{\partial \tilde{a}^{(p),res}(\rho, T, x_i, x_p)}{\partial x_i}\right|_{x_i=0,x_p=1} - \tilde{a}^{(p),res}(\rho_g^0, T) - Z^{(p)}(\rho_g^0, T) - \ln(\rho_g^0 kT) \tag{20}$$

where the units of S_0 are given in $mol/[mol_{pol}atm]$, Z is the compressibility, ρ represent the total number density, the superscript p represents the polymer phase, and the subscripts i and p represent the sorbent and the glassy polymer respectively. However, unlike the NELF model, we have found that the S_0 approach can lead to inadequate parameters for the NE-PC-SAFT. This may be due to the highly non-linear nature of the NE-PC-SAFT equation, especially in comparison to the S_0 expression given by the NELF model. Alternatively, one can simultaneously regress the pure parameters and binary interaction parameter directly to the sorption isotherms [59,61]. Therefore, for cases where PVT data are available, the objective function of the optimization procedure becomes:

$$\min_{m_p,\sigma_p,\epsilon_p} \sum_l \left(\frac{\rho_{pol,l}^{exp.} - \rho_{pol,l}^{calc.}}{\rho_{pol,l}^{exp.}}\right)^2 \tag{21}$$

On the other hand, when only sorption data are available, the objective function is:

$$\min_{m_p,\sigma_p,\epsilon_p,\{k_{ip}\}} \sum_l \sum_i \left(\frac{\Omega_{i,l}^{exp.} - \Omega_{i,l}^{calc.}}{\Omega_{i,l}^{exp.}}\right)^2 \tag{22}$$

where l is the experimental data point, i is the sorbent species, $exp.$ stands for the experimental value, $calc.$ stands for the calculated value, and Ω is the sorption of species i in the polymer. It is worth noting that at least two sorbent species must be used when Eq. (22) is applied to obtain a more generalizable set of parameters. In addition, the polymers investigated herein are non-self associating, hence, only the non-associating parameters are regressed to the experimental data.

3. Results and discussion

3.1. Estimating the PC-SAFT pure polymer parameters and modeling light gas sorption in glassy polymers

In this work, the sorption in 8 glassy polymers will be investigated. Rubbery PVT data at various temperature and pressure conditions are available for poly(methyl methyacrylate) (PMMA) [86] and Cytop [87], which were used to obtain the pure PC-SAFT parameters for both polymers. The results of the PMMA fitting procedure are shown in Fig. 2. PIM-1, PIM-EA-TB, Matrimid, 6FDA-mPDA, 6FDA-4-4'-pAPPP and PTMSP, on the other hand, lack pure PVT data. Hence, the sorption isotherms of light gases were used to fit the parameters (except for PTMSP's pure parameters, which was fitted to propane's and n-butane's sorption isotherms. The reason for this decision will be explained in Section 3.3). Light gas sorption data, particularly for CO_2, CH_4, and N_2 are the most abundant in literature. Hence, testing the viability of the pure parameters estimated from these isotherms using the DGRPT model is important, since for a lot of the high T_g polymers, they may be the only data available.

For each of the high T_g polymers listed above, two light gas sorption isotherms were used in the parameterization scheme. The type of the sorption isotherms used for each of the polymers, their pure parameters and the resultant binary interaction parameter (k_{ip}) values for the selected gases are reported in Table 2, while Fig. 3 showcases the first order DGRPT calculations of the sorption isotherms based on these parameters. The small magnitudes of the k_{ip} values of the fitted isotherms indicates the reliability of the estimated polymer parameters. However,

Table 2
The list of the pure non-associating PC-SAFT parameters, the volumetric thermal expansion coefficients (α_v), the binary interaction parameters (k_{ip}), and the dry densities (ρ_g^0) for the polymers investigated.

Polymer	m/M_w ($\frac{mol}{g}$)	σ (Å)	ϵ/k (K)	α_v (K^{-1})	Fitted to[a]	k_{1p}	k_{2p}	$\rho_g^{0,b}$ ($\frac{g}{cm^3}$)
PMMA	0.035	3.28	297.14	5.1E−4 [89]	PVT [86]	–	–	–
Cytop	0.015	3.54	234.34	2.6E−4 [90]	PVT [87]	–	–	–
PIM-1	0.044	2.92	293.80	–	(1) CH_4 [15], (2) N_2 [15]	0.022	0.007	1.10(25 °C) [23]
PIM-EA-TB	0.047	2.81	282.58	–	(1) CO_2 [16], (2) CH_4 [16]	0.070	−0.065	1.13(25 °C)[16]
Matrimid	0.048	2.81	321.50	8.4E−05 [91]	(1) CO_2 [17], (2) CH_4 [17]	0.100	0.090	1.23(23 °C) [17]
6FDA-mPDA	0.049	2.67	348.60	2.0E−04 [48]	(1) CO_2 [88], (2) CH_4 [88]	0.052	−0.033	1.47(23 °C) [88]
6FDA-4-4′-p-APPP	0.048	2.81	450.00	2.0E−04 [48]	(1) CO_2 [92], (2) CH_4 [92]	0.100	0.028	1.35(25 °C)[92]
PTMSP	0.038	3.44	226.80	–	(1) C_3H_8 [93], (2) C_4H_{10} [93]	0.003	0.012	0.75(35 °C)[93]

[a] The number on the left hand side of the gas used for sorption regression indicates which k_{ip} value belongs to it.
[b] The dry density quantities indicated in this table are used for the sorption regression procedure to obtain the PC-SAFT parameters. Different density values may be used for other sorption calculations for the same polymer in this paper, which depends on the sample's history.

to truly test the transferability of the pure polymer parameters, the quality of fit and the k_{ip} of some gas isotherms that did not participate in the parameterization process must be evaluated.

For PIM-1, CO_2 sorption [15] was not involved in the fitting procedure, similarly, for PIM-EA-TB [16] and 6FDA-mPDA [88] the N_2 sorption isotherms were not used. For each of these gases, the k_{ip} parameters were fitted to their sorption isotherms,resulting in the k_{ip} values of 0.088, −0.065, and −0.118 for PIM-1, PIM-EA-TB, and 6FDA-mPDA respectively. From Fig. 3(a) and (c), its evident that the quality of fit of these isotherms is good, and it was achieved with a minor correction to the cross energetic parameter based on the low magnitude values of k_{ip}.

Overall, the first order DGRPT model results show a very good quality of fit to the light gases isotherms investigated here. Generally speaking, N_2 is a weak swelling agent. Hence, the NET-GP theory alone can provide a set of equations that can adequately model the N_2 solubility without the need of a swelling model. On the other hand, CH_4 sorption can moderately dilate the polymer, particularly at high pressures, which necessitates the incorporation of the swelling effects into the NET-GP framework. The first order DGRPT seems to be appropriate for such applications. On the contrary, CO_2 sorption can be a strong swelling agent. For the cases explored in this section, the accuracy of the CO_2 sorption modeled by the DGRPT is good. This is because of the Langmuir-like behaviors that these isotherms exhibit. Thus, for all of the isotherms modeled in Fig. 3, the first order DGRPT becomes a single parameter (i.e. k_{ip}) model.

However, in some CO_2 sorption isotherms, such as in PMMA [94], the gas uptake behaves linearly with respect to pressure, particularly at higher loadings. For cases like this, the second order DGRPT becomes more suitable to accurately capture the sorption trend.

3.2. Application of the second order DGRPT to isotherms exhibiting linear/dual mode behaviors

3.2.1. Co_2 sorption in PMMA

Originally developed for high free volume polymers, the first order DGRPT has been shown to lose accuracy when modeling the sorption of CO_2 in dense materials with a linear dependence on pressure like in the case of PMMA [70]. In the second order DGRPT introduced here, the second-order parameter (γ_{ii}) can be adjusted to the sorption isotherm to account for the swelling effects occurring at higher pressures. Fig. 4 reports the DGRPT calculations with (i.e. second order theory) and without (i.e. first order theory) this parameter. Unlike the previously modified version proposed by Marshall [70], the additional swelling effects were delegated to the second-order terms rather than the first. Hence, a weaker dilation response occurs at the lower end of the pressure range, and a Langmuirian behavior is observed at lower pressures. As the pressure increases, the calculated isotherm becomes linear, resulting in a more accurate description of the sorption behavior. The density of the PMMA sample was set to 1.188 g/cm^3 at ambient conditions (i.e. 25 °C and atmospheric pressure) as reported by Raymond and Paul [94]. The dry density at 35 °C was obtained using the thermal expansion coefficient value (α_v) reported in Table 2. Overall, a marked improvement of the DGRPT's accuracy can be observed with the inclusion of γ_{ii} as shown in Fig. 4.

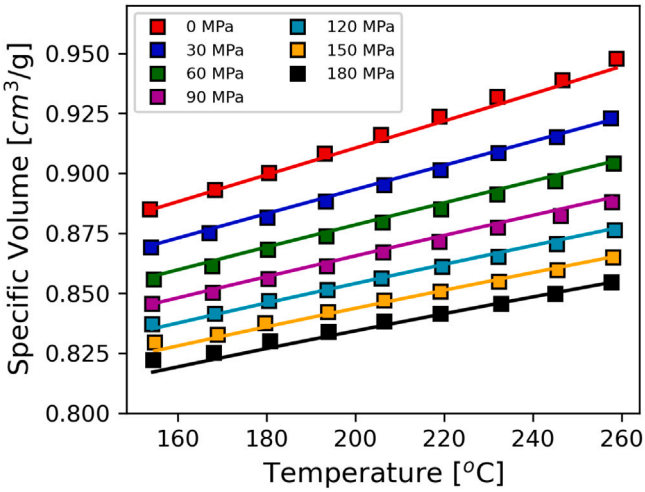


Fig. 2. The PC-SAFT EoS calculations for the Poly(Methyl Methacrylate) PVT behavior. Discrete points represent the experimental data [86], while the continuous curves are the model's calculations.

3.2.2. Understanding the sorption effects of the second-order parameters

As mentioned in Section 2.3, the second-order parameter γ_{ii} defines the total second-order derivatives of the polymer's chemical potential and density at infinite dilution. Fig. 5(a) shows how decreasing γ_{ii} leads to an increase in the CO_2 uptake in PMMA, with the effects getting stronger at the higher end of the pressure range. This is due to the fact that a negative γ_{ii} leads to a negative total second-order derivative of μ_p (see Fig. 5(b)). In this case, the second-order correction results in a lower polymer chemical potential in comparison to the first-order DGRPT, and thus, a lower polymer composition (i.e. by increasing sorption).

3.2.3. Utilizing temperature independent second-order parameters: Gas sorption in PIM-1 and Cytop at various temperatures

In systems where multiple sorption isotherms at different temperatures are available, a single temperature independent γ_{ii} can be used to describe isotherms exhibiting dual-mode/linear sorption behavior. To showcase this feature of the second-order DGRPT, we will explore the solubility of propane in PIM-1 and the solubility of CO_2 in Cytop. The dry densities used for the calculations are 1.1 g/cm^3 at 25 °C [23] and 2.022 g/cm^3 at 22 °C [95] for PIM-1 and Cytop, respectively. The dry densities of the polymer samples at different temperatures

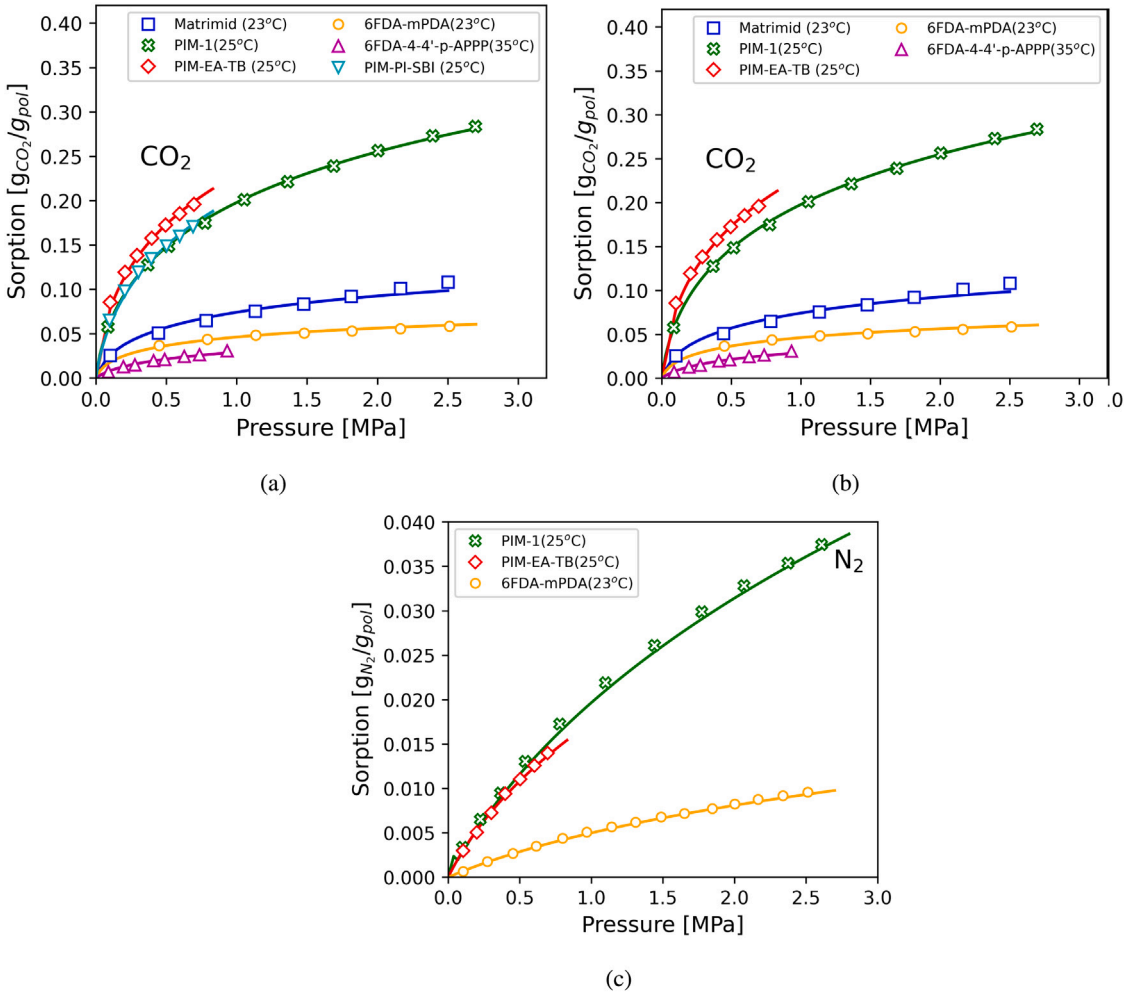


Fig. 3. First-order DGRPT modeling results of (a) CO_2, (b) CH_4, and (c) N_2 sorption in Matrimid [17], PIM-1 [15], PIM-EA-TB [16], 6FDA-mPDA [88], and 6FDA-4-4'-p-APPP [92]. Discrete points represent the experimental data, while the continuous curves are the model's predictions.

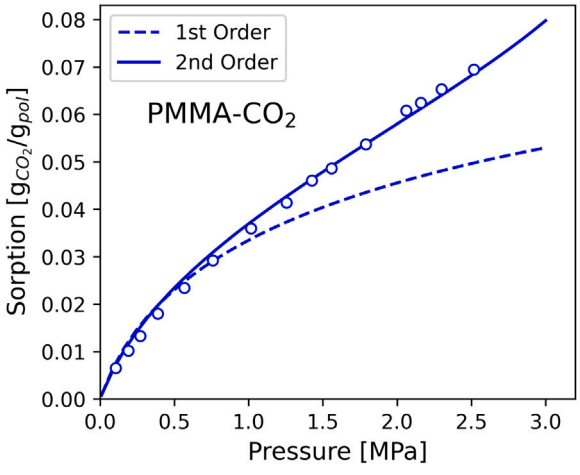
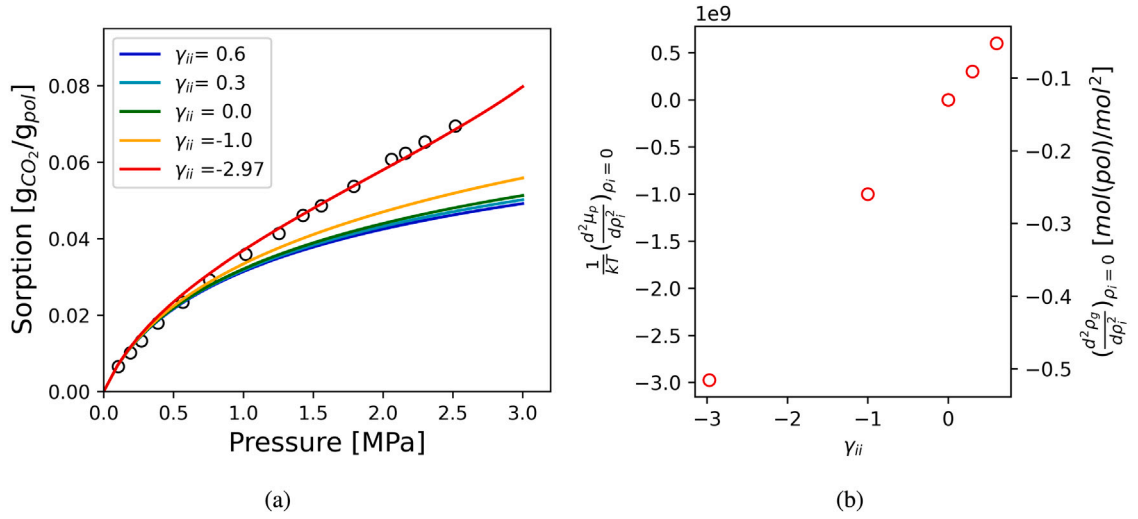


Fig. 4. First and Second DGRPT calculations for the sorption of CO_2 in PMMA at 35 °C. Experimental data shown as discrete points are taken from Ref. [94]. The fitted parameters for the second order theory are $k_{ip} = -0.0312$, $\gamma_{ii} = -2.97$ and $k_{ip} = -0.0378$ for the first order theory.

Table 3
The fitted parameters for the sorption of propane in PIM-1 and CO_2 in Cytop.

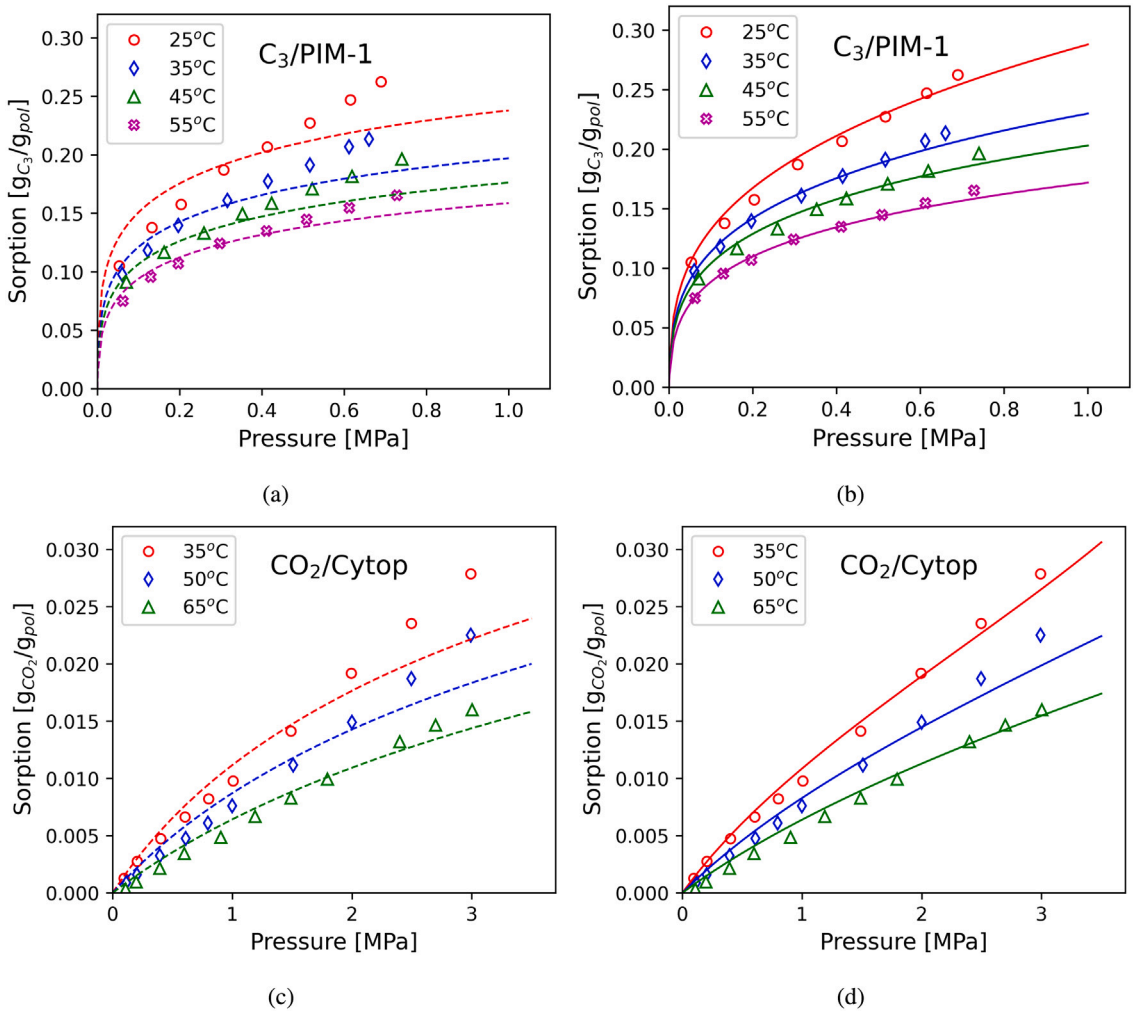
Polymer	k_{ip} (T/°C)	γ_{ii}
PIM-1 (first order)	$-6.90\ T \times 10^{-4} + 0.0724$	0.0
PIM-1 (second order)	$-1.80\ T \times 10^{-3} + 0.1537$	−0.1
Cytop (first order)	$3.00\ T \times 10^{-4} + 0.0730$	0.0
Cytop (second order)	$6.67\ T \times 10^{-5} + 0.0923$	−3.8

were obtained using the thermal expansion coefficients reported in Table 2. The results of the DGRPT calculations are shown in Fig. 6 for both the first- and second-order theories. For each system, a single γ_{ii} was obtained by fitting to the lowest temperature isotherm, then, the k_{ip} values of the other isotherms was adjusted to fit the curves more appropriately. The values of these parameters are reported in Table 3. As can be observed in Fig. 6, the second-order theory had improved the quality of fit of the isotherms, particularly at the higher pressure ranges. Interestingly, the first-order form of the DGRPT seems to perform better as the temperature is increased. Another noteworthy observation is that as you decrease the value of γ_{ii}, a higher k_{ip} is often required to fit the data, which is a trend that will be observed throughout this work.



(a) (b)

Fig. 5. (a) The effects of γ_{ii} on the CO_2 sorption in PMMA at 35 °C with k_{ip} = −0.0312. The experimental data shown as dots are taken from Ref. [94]. (b) Effects of γ_{ii} on the second-order derivatives at infinite dilution.



(a) (b) (c) (d)

Fig. 6. A comparison of the performance of the first order DGRPT against the second order theory for (a & b) the sorption of propane in PIM-1 and (c & d) the sorption of CO_2 in Cytop. First and second order results are shown as the dash and continuous curves respectively, while the experimental data are the discrete points.
Sources: Experimental data are taken from Ref. [96] for PIM-1 and Ref. [90] for Cytop.

Table 4
The number of associating sites, the mixture parameters, and the dry polymer densities used for the alcohol sorption calculations. 'MeOH', 'EtOH', and 'PrOH' stand for methanol, ethanol and 1-propanol respectively.

Polymer	n_a	MeOH			EtOH			PrOH			ρ_g^0 ($\frac{g}{cm^3}$)
		k_{ip}	γ_{ii}	$\kappa_{A_pB_p}$	k_{ip}	γ_{ii}	$\kappa_{A_pB_p}$	k_{ip}	γ_{ii}	$\kappa_{A_pB_p}$	
PIM-1	17.37E−3M_w	0.100	0.0	0.005	0.124	−0.02	0.005	0.145	−0.04	0.005	1.10 [26]
PIM-EA-TB	13.00E−3M_w	0.110	0.0	0.003	0.050	0.0	0.003	0.105	−0.05	0.003	1.13 [16]
Matrimid[a]	18.00E−3M_w	0.028	−0.1	0.035	0.060	−0.22	0.0324	0.100	−0.48	0.015	1.23 [17]

[a] Since the Matrimid data was measured at 30 °C, the dry density value was corrected using α_v = 8.40E−05 K^{-1}. The initial values of the dry polymer densities provided in this table were assumed to be at 25 °C.

3.3. Modeling the sorption of alcohols in glassy polymers

Modeling the sorption of alcohols accurately often necessitates the use of the hydrogen bonding term given in Eq. (14). Marshall et al. [61] were able to successfully model the rather anomalous sorption behaviors of alcohols in PTMSN [60,97] using the sPC-SAFT and the first order DGRPT model, with each alcohol molecule given a single hydrogen donor site (n_d) and two hydrogen acceptor sites (n_a) (i.e. the 3B model [98]). In this work, we have found that the 2B model (i.e. $n_d = n_a = 1$) is also capable of modeling the sorption isotherms of alcohols in glassy polymers accurately.

Starting off with PTMSP, a polymer known for its high free volume and hydrophobic nature, a uniquely sigmoidal shaped isotherm can be observed for alcohols as shown in Fig. 7(b). This may be attributed to the relative weakness of the sorbent-to-polymer interactions in comparison to the sorbate-to-sorbate interactions, which may eventually result in clustering.

The pure PC-SAFT parameters of PTMSP were obtained by regressing to the isotherms of propane and n-butane alongside the binary interaction parameters and using a dry polymer density of 0.75 g/cm^3 [93]. The values of the parameters are reported in Table 2 and the regressed isotherms are shown in Fig. 7(a). We note that while Marshall et al. [61] have reported a set of PTMSP parameters, those parameters were not suitable for fitting the isotherms reported by Nakanishi et al. [29] due to the difference of the dry density value used by Marshall et al. during parameterization (which was 0.8 g/cm^3). Indeed, the utility of the parameters regressed to sorption data alone is highly dependent on the dry density value used, which might be one of the limitations of this approach. Thus, the parameters of PTMSP were obtained here by fitting the solubility data of PTMSP at a measured density similar to the value reported by Nakanishi et al.

Since the structure of the PTMSP's repeat unit lacks lone electron pairs, the polymer would not be allowed to cross associate with the vapor. Thus, $\epsilon_{A_iB_p}$ and $\kappa_{A_iB_p}$ are set to zero. Using the first-order form of the DGRPT, a good fit to the methanol and the ethanol isotherms can be achieved with k_{ip} values of 0.045 and 0.065 respectively as shown in Fig. 7(b).

In the cases of PIM-1, PIM-EA-TB, and Matrimid, the alcohol sorption isotherms exhibit the conventional concave shape seen in other classes of sorbates. However, at higher activities, an upturn in the isotherm, probably caused by a combination of a sorption induced glass transition and clustering, can be observed [21,23,99], leading to an inverse S shaped isotherm. Since the DGRPT is a model for glassy polymers, we will only fit the isotherms in the regions before the upturn is observed (i.e. before the sorption-induced glass transition). These polymers do not self-associate, nevertheless, in the presence of associating vapors, the lone electron pairs found in some chemical groups, such as the carbonyl groups in Matrimid, can interact with the associating vapor. To account for this 'induced association', the following approach, based on the method introduced by Kleiner and Sadowski [100], will be used in this work:

- Lone electron pairs found in each polymer segment will be assigned a hydrogen donor site, and a hydrogen acceptor site. Since the polymers do not self-associate, the hydrogen bonding energetic parameter ($\epsilon_{A_pB_p}$) will be set to zero. Table 4 reports the total number of sites in each polymer as a function of the molecular weight (M_w).
- To account for the induced association interactions, the cross volume of bonding $\kappa_{A_iB_p}$ must be determined. Kleiner and Sadowski [100] suggested equating the volume of bonding of the polymer ($\kappa_{A_pB_p}$) to that of the vapor ($\kappa_{A_iB_i}$), $\kappa_{A_iB_p}$ is then calculated using Eq. (19). This pragmatic assumption avoids the need to fit $\kappa_{A_pB_p}$ to mixture data. However, in certain cases, this assumption can lead to high k_{ip} values, thus the $\kappa_{A_pB_p}$ value was lowered accordingly. The values of $\kappa_{A_pB_p}$, alongside the DGRPT parameters, are all reported in Table 4.

Fig. 7(c) showcases the comparison between the modeling results of the first- and second-order theories, respectively, for the methanol-Matrimid system, where a marked improvement in the model's performance is observed, particularly at the high-activity region of the isotherm. Overall, a good quality of fit to the methanol, ethanol and 1-propanol isotherms in the glassy region for all three polymers is achieved by the second order DGRPT as shown in Fig. 8.

3.4. Water sorption in glassy polymers

The presence of water in the system can introduce some modeling challenges. Using the Wolbach and Sandler combining rules and the induced association approach proposed by Kleiner and Sadowski [100] often leads to unsatisfactory results when working with the NET-GP framework. Nevertheless, Liu and Kentish [43] and Borrmann et al. [44] showed that a decent description of the isotherm can be achieved through the equilibrium PC-SAFT. The justification for this choice was based on the conjecture that the influences of the microvoids found in glassy polymers are minimal in comparison to those of the hydrogen-bonding interactions of water. In this work, we will use a different approach when dealing with water isotherms. As discussed earlier, PTMSP does not cross-associate, hence, the hydrogen bonding interactions are only occurring between the water molecules. Fig. 9 showcases the results of the first order DGRPT calculations using the 2B parameters of water [84]. Clearly, the convex shape of the water isotherm was captured without having to resort to using the equilibrium version of the PC-SAFT EoS. We speculate that the Wolbach and Sandler combining rule may be inadequate in representing the cross-association interactions between water and glassy polymers. As a result, the following approach will be used:

- Similar to the alcohol case, the polymer molecule will also be assigned a hydrogen acceptor and donor sites per associating group in its monomers.
- The energetic hydrogen bonding parameter $\epsilon_{A_pB_p}$ of the polymer will be set to zero, allowing the cross energetic parameter $\epsilon_{A_iB_p}$ to be calculated through Eq. (18). The cross volume of hydrogen bonding $\kappa_{A_iB_p}$ will then be adjusted to the sorption data.
- $\kappa_{A_iB_p}$ will be treated as a temperature-independent parameter. Hence, once determined using a single isotherm, the model can fit the other isotherms using k_{ip} alone, which corrects for the dispersion cross energetic interactions.

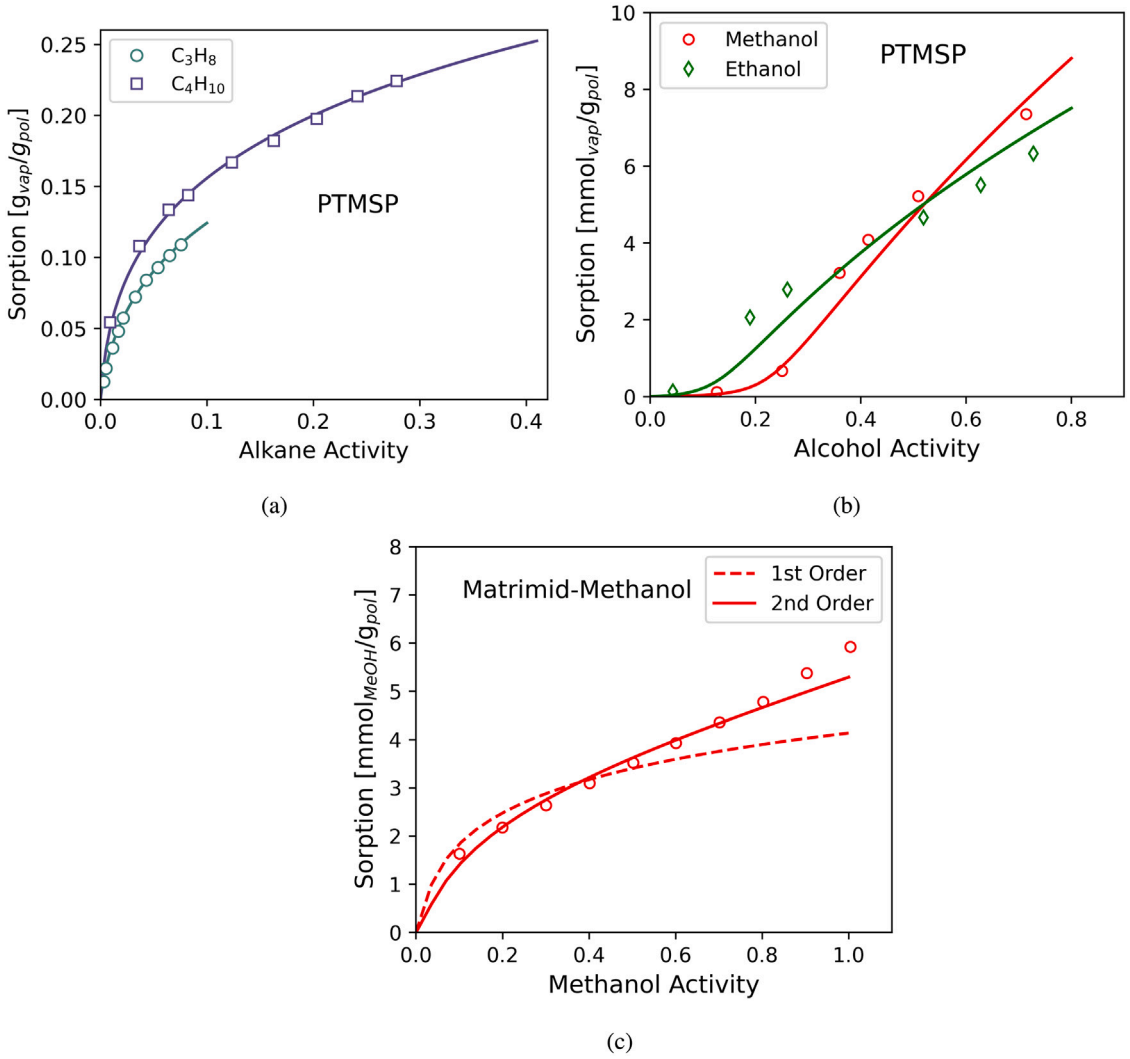


Fig. 7. (a) A comparison of the calculated isotherms to the experimental propane and n-butane data [93] for PTMSP using the first order DGRPT.The Isotherms were measured at 35 °C (b) A comparison of the first-order DGRPT calculations to the experimental alcohol sorption data at 25 °C for PTMSP [29]. (c) A comparison of the first and second order DGRPT calculations to the experimental methanol sorption data at 30 °C in Matrimid [99]. The parameters of the second order theory for methanol-Matrimid are reported in Table 4, while the first order parameters are $k_{ip} = -0.01$ and $\kappa_{A_pB_p} = 0.035176$.

Fig. 10 shows the modeling results for the water sorption in PMMA, Matrimid, 6FDA-mPDA, and 6FDA-4-4'-p-APPP. In all of these cases, $\kappa_{A_iB_p}$ was fitted simultaneously with k_{ip} at the lowest temperature isotherm, then, by keeping $\kappa_{A_iB_p}$ constant, k_{ip} alone was adjusted to the other isotherms. The optimized parameters, along with the dry density values used for the DGRPT calculations, are shown in Table 5. All dry densities were assumed to be reported at 25 °C and the dry densities values at different temperatures were corrected using the volumetric thermal expansion coefficients reported in Table 2. As it can be seen from Fig. 10, this methodology resulted in a good quality of fit to the water isotherms explored here.

Table 5
The number of associating sites, the mixture parameters and the dry polymer densities used for the water sorption calculations.

Polymer	n_a	$\kappa_{A_iB_p}$	k_{ip} (T/°C)	ρ^0_{pol} ($\frac{kg}{m^3}$)
PTMSP	0.0	0.0	$4.54\ T \times 10^{-3} - 0.1274$	0.75 [93]
PMMA	$0.020*M_w$	0.041	$-7.60\ T \times 10^{-4} + 0.0197$	1.20 [102]
Matrimid	$0.018*M_w$	0.105	$-2.00\ T \times 10^{-4} + 0.1957$	1.24 [27]
6FDA-mPDA	$0.085*M_w$	0.019	$-4.00\ T \times 10^{-4} + 0.1530$	1.47 [103]
6FDA-4-4'-p-APPP	$0.059*M_w$	0.0214	$-2.00\ T \times 10^{-4} + 0.2057$	1.35 [103]

4. Conclusion

The NET-GP framework developed by Doghieri and Sarti [24] laid the foundations for describing the pseudo-equilibrium conditions found between a glassy polymer membrane and the external fluid. By leveraging the power of equations of state, the sorbent loading can be calculated accurately by virtue of the analytical forms of the chemical potential. In the years that followed, Marshall et al. [61] proposed the DGRPT as a method to represent the swelling in glassy polymers.

While successful in representing Langmurian-type isotherms, the DGRPT's accuracy reduces when dual mode sorption-like isotherms of plasticizing sorbents are encountered. In the modification that we have introduced here, the DGRPT was able to ameliorate this issue by introducing a second-order correction to the polymer's chemical potential, dictated by the second order parameter γ_{ii}. γ_{ii} can be treated as a temperature-independent parameter, thus requiring only the adjustment of k_{ip} for the other temperature conditions.

When it comes to the PC-SAFT EoS, representing the associating interactions reliably plays a critical role in the overall performance of the model. Different parameterization schemes for the cross-association

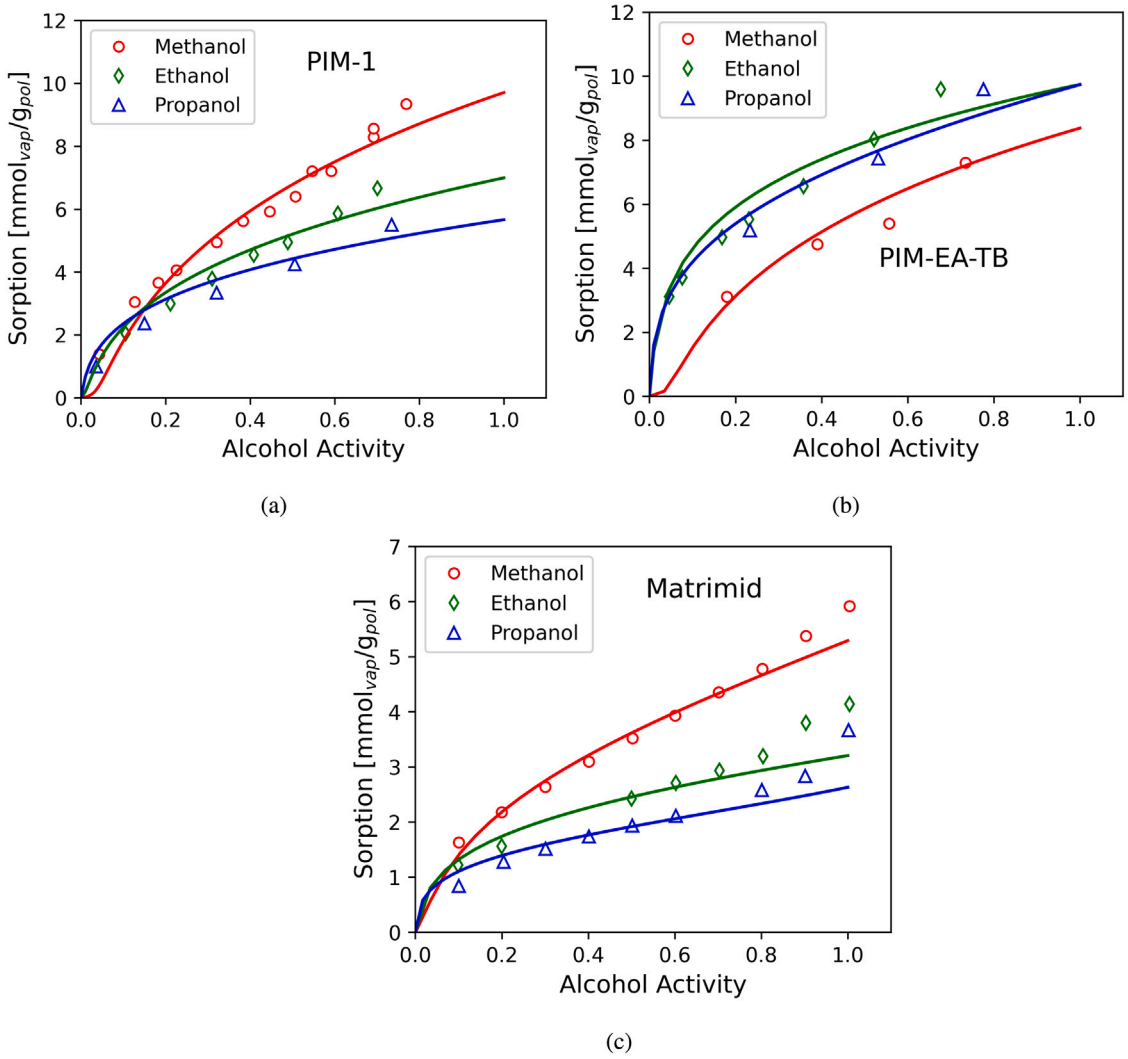


Fig. 8. The second order DGRPT calculations for the sorption of methanol (MeOH), ethanol (EtOH), and 1-propanol (PrOH) in (a) PIM-1 at 25 °C, (b) PIM-EA-TB at 25 °C, and (c) Matrimid at 30 °C.
Sources: Experimental data shown as discrete points are taken from Ref. [21,23,99].

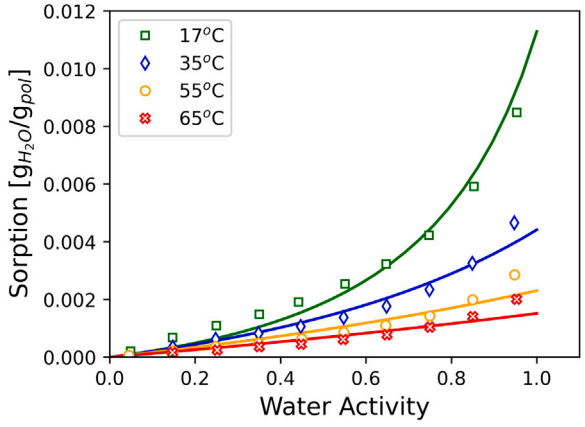


Fig. 9. Sorption of water in PTMSP modeled by the first-order DGRPT at different temperatures.
Source: Experimental data are taken from ref [101].

interactions between the vapor and the glassy polymer were considered. For the systems investigated here, we have found that alcohol sorption can be represented remarkably well with the induced association approach introduced by Kleiner and Sadowksi [100], however, a reduction in the polymer association interactions may be required for obtaining reasonable values for k_{ip}. On the contrary, cross association interactions between water and the glassy polymer required fitting the cross association parameters to the mixture data. In this work, $\kappa_{A_iB_p}$ was treated as an extra adjustable parameter and $\epsilon_{A_pB_p}$ was set to zero. In this parameterization procedure, $\kappa_{A_iB_p}$ was also considered as a temperature independent parameter, hence, once fitted to a single isotherm, the other isotherms can be modeled adequately by varying k_{ip} alone for the same polymer.

In principle, there are no restrictions on the type of the equation of state that can be applied within the DGRPT formalism, provided that it can adequately represent the vapor-polymer system in question. For instance, other popular equations of state, like the LF and NRHB models can be used within this framework. Nevertheless, the strength of the NET-GP approach and its variants comes from its predictive capabilities. In our upcoming work, we will demonstrate the use of the modified DGRPT in the prediction of mixed gas sorption and the variation of the solubility of the gas as a function of the copolymer's

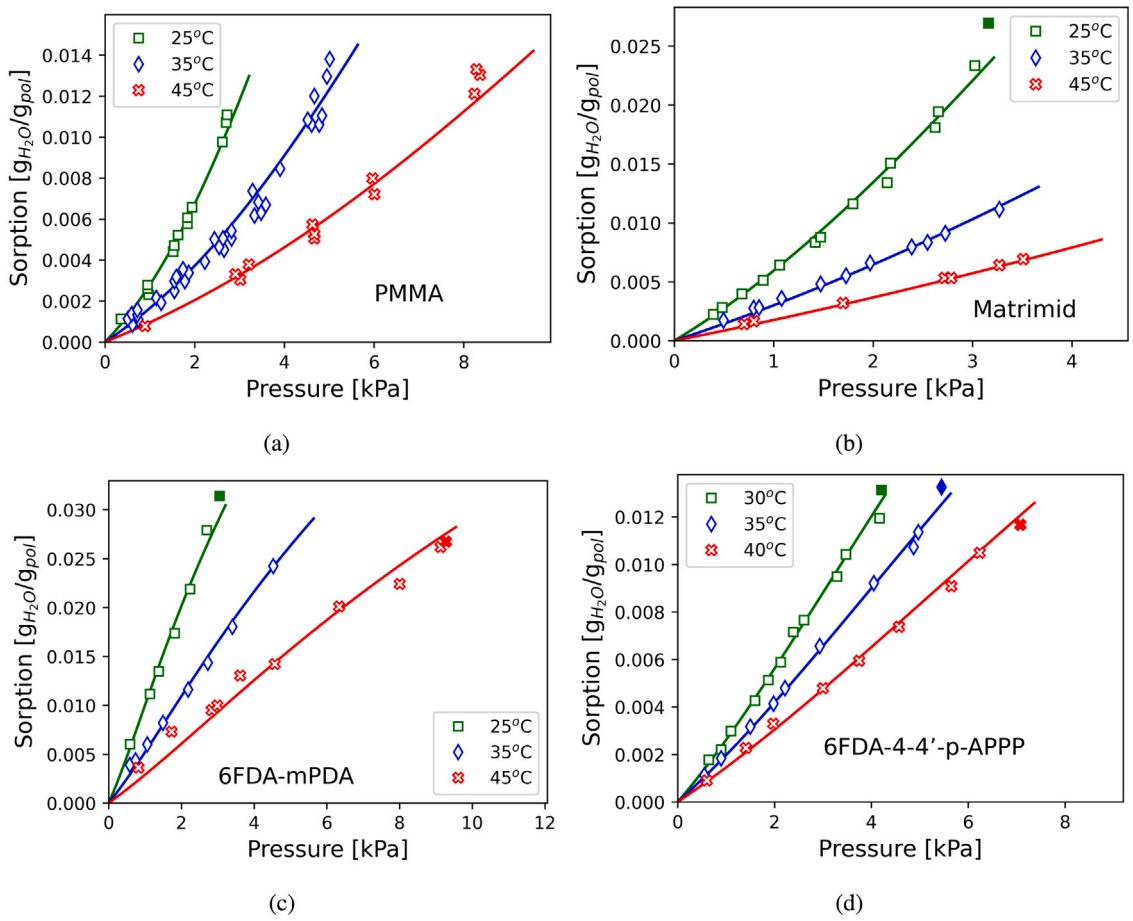


Fig. 10. A comparison between the first-order DGRPT calculations and the experimental data for the water sorption in (a) PMMA [102], (b) Matrimid [27], (c) 6FDA-mPDA [103] and (d) 6FDA-4-4'-p-APPP [103]. Modeling results are shown as the continuous curves, while the experimental data are the discrete points. The filled points indicate condensation.

monomer composition. Both of the formerly mentioned properties can be essential in the selection and the discovery of novel polymeric materials for such applications.

CRediT authorship contribution statement

Hasan Ismaeel: Writing – original draft, Software, Methodology, Data curation, Conceptualization. **Bennett D. Marshall:** Writing – review & editing, Supervision, Software, Methodology, Data curation, Conceptualization. **Eleonora Ricci:** Writing – review & editing, Supervision, Software, Methodology, Data curation, Conceptualization. **Maria Grazia De Angelis:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Data curation, 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.

Acknowledgment

We gratefully acknowledge financial support from the Royal Society of Edinburgh (RSE) under grant award 2915 for the project titled "A Machine Learning-Aided Modeling Platform for the Design of Hydrogen-Ready Materials".

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.fluid.2025.114410.

Data availability

Data will be made available on request.

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