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Cryogenic gas sorption in high free volume glassy polymers: thermodynamic modeling and permeability correlations

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ABSTRACT

Understanding the relationship between polymer structure, free volume, and gas-transport properties remains a central challenge in the design of membrane materials. In this concern, the fractional free volume (FFV), first outlined by Bondi's theory, is considered as the unoccupied space between the polymer chains in which the molecules of the penetrant gas can be accommodated.

In recent years, the use of cryogenic N_2 sorption in polymers has gained significant popularity for the characterization of gas separation membrane materials. In this work, cryogenic measurements, BET analysis, and the use of Equation of State (EoS) thermodynamic models are combined to establish a unified framework for quantifying free volume and its role in governing permeability. A wide range of polymer families is considered, including high-free-volume materials, the so-called intrinsically microporous systems, and conventional commercial polymers. Nitrogen sorption isotherms at 77 K provide experimentally accessible descriptors to estimate the polymer fractional free volume and to capture differences in backbones accessibility and polymer swellability. Furthermore, the FFV is evaluated by means of the Non-Equilibrium Lattice Fluid (NELF) model, which relates sorption behavior to the characteristic density of the polymer-penetrant system. The FFV values derived from NELF and from N_2 sorption analysis show close agreement, indicating that cryogenic sorption data offer a reliable measure of thermodynamically accessible free volume.

These parameters correlate well with gas permeability, demonstrating that low-temperature sorption can be effectively used to probe the free-volume architecture of dense polymers, i.e. in systems lacking well-defined porosity.

1. Introduction

Over the past decades, an extensive amount of data on the permeation of gases such as helium, hydrogen, oxygen, nitrogen, methane, and carbon dioxide in a wide array of glassy polymers has been reported. Much of this work has been motivated by the search for materials with high permeability and high selectivity for potential use as gas separation membranes [1–5].

Within this context, membrane separation technologies represent a particularly promising approach, offering a more sustainable alternative to conventional separation processes, such as adsorption, solvent absorption, and distillation. Polymeric membranes stand out due to their low energy requirements, operational simplicity, and reduced environmental impact [2,6].

Despite these advantages, large-scale industrial implementation still faces challenges: achieving high product purity frequently requires multiple stages, and material limitations often constrain the attainable balance between permeability and selectivity [7,8]. There is an important need to understand the physical rationale that governs the relationship between gas permeability and polymer repeating unit structure and resulting architecture: such a predictive tool may be useful for guiding the development of new polymers. In this regard, the fractional free volume (FFV), defined as the fraction of unoccupied space between polymer chains [9], is probably the most accepted metric for describing the diffusivity of small molecules in polymers.

Such parameter is particularly relevant in glassy polymers, where the amount, distribution, and connectivity of free-volume elements strongly influence gas solubility, diffusivity, and ultimately permeability [10,11]. Although direct experimental measurement of FFV is challenging, the FV theory remains a valuable predictive tool applicable to polymeric

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system both above and below the glass transition temperature (T_g).

The first systematic attempts to estimate polymer free volume trace back to van der Waals-based volume calculations [12]. In *Properties of Polymers* (1972), Van Krevelen [13] extended Bondi's earlier group contribution approach to predict polymer volumetric properties in the absence of direct experimental data [14]. He reported that, according to Bondi, the zero-point molar volume (V^0 (0)) could be approximated as 1.3 times the van der Waals volume (V_{VdW}); however, the physical basis of this empirical factor remained unclear.

Building upon this work, Lee [15] was the first to explicitly employ Van Krevelen's relationship to estimate polymer free volume. His study marked the integration of group contribution methods with free-volume theory, providing a simple route to link molecular structure with macroscopic transport properties.

While early free-volume theories by Bondi, Van Krevelen and Lee provided empirical correlations between molecular structure and occupied volume, with the development of solid molecular modeling approaches, available to describe the behavior of polymeric materials (as interestingly reviewed by Fermeglia's group [16]), new studies have extended these concepts targeting the direct investigation of free volume pockets in glassy matrices of different structures [17–20].

Such theoretical framework directly underpins modern interpretations of gas transport in high-free-volume glassy polymers, where inefficient chain packing and non-equilibrium microstructures yield exceptional permeabilities, often approaching the Robeson's upper bound [8,21]. In these non-equilibrium materials, molecular transport proceeds through transient, dynamically accessible voids formed during the material cooling process in which part of the free volume available in the polymeric structure remains frozen in it as excess free volume. Under these conditions, the Gibbs phase rule of equilibrium does not hold true [22,23]. Consequently, the diffusion and sorption behavior of small, weakly interacting penetrant molecules in glassy polymers is commonly understood to be primarily governed by free-volume characteristics, due to their direct impact on molecular mobility [13].

Park and Paul [24], employing a group contribution approach to estimate the free volume of rigid-backbone glassy polymers and to provide suitable expressions for gas permeability data, showed that FFV-based correlations are not limited to a specific polymer class, but instead reflect a more general structure-property relationship. Establishing reliable correlations between these structural parameters and the macroscopic transport properties of gases is essential for both material design and model development.

The experimental investigation of these ultra-high free-volume materials often includes cryogenic gas sorption measurements, most commonly with nitrogen or argon at their normal boiling temperatures (77 K and 87 K, respectively) [18,25–27,27–33]. The methodology is analogous to that used for traditional microporous sorbents such as zeolites, activated carbons, or metal-organic frameworks (MOFs), where adsorption occurs on a well-defined internal surface. In both cases, the shape of the sorption isotherm reflects the distribution and accessibility of the unoccupied regions within the material. For rigid porous solids, the analysis of these isotherms using the Brunauer-Emmett-Teller (BET) theory yields meaningful physical quantities, such as surface area and pore size distribution [34]. As already pointed out by Minelli et al. [25,26], the same approach has often been extended to glassy polymers, adopted to obtain comparative parameters, despite the absence of permanent porosity or a clear continuous network of pores. In this context, the BET-derived surface area does not represent a true geometric property, but rather it may serve as an empirical indicator of the extent of accessible free volume that can accommodate gas molecules. Thus, the application of BET analysis to high-free-volume polymers can provide phenomenological correlations between molecular-level free-volume features and macroscopic transport behavior, even if the underlying physical mechanisms differ fundamentally from those in rigid porous adsorbents.

However, the direct application of the BET theory to glassy polymers, defined as being in a frozen-like state, remains conceptually controversial. In these systems, unoccupied regions, which can be viewed as a dispersed "void phase" within the polymer bulk, are not permanent or interconnected pores, but rather transient and irregular free-volume elements, originated from inefficient chain packing and the inherently non-equilibrium nature of the glassy state [22,35–37].

Consequently, parameters derived from BET analysis may not correspond to physically meaningful surface areas or pore dimensions. That raises the question of whether the physical interpretation underlying the BET model - based on adsorption onto a rigid surface - can legitimately be extended to non-equilibrium amorphous solids. At cryogenic temperatures, such as N_2 at 77 K, gas sorption is therefore better interpreted in terms of absorption (physical dissolution) and matrix deformation rather than classical surface adsorption phenomena.

Therefore, in order to interpret the experimental results originated from crygenic gas sorption analysis and to correlate the FFV data obtained with volume dilation and density in such conditions, non-equilibrium thermodynamic model may be conveniently employed to describe gas sorption and diffusion in glassy materials. In particular, the Non-Equilibrium Thermodynamic model for Glassy Polymers (NET-GP), developed by Doghieri and Sarti in 1996 [38,39], has been successfully used to interpret gas uptake in a wide range of polymers, from conventional glassy systems to high-FFV materials such as polymers of intrinsic microporosity (PIMs), poly(trimethylsilyl propyne) (PTMSP), and modified polyimides (PI) [25,26,40,41]. The extension of Lattice Fluid equation of state for Non-Equilibrium system (NELF) treats the glassy polymer matrix as a homogeneous out of the equilibrium phase characterized by its macroscopic density, without requiring detailed knowledge of local structural heterogeneity [40,42,43]. The model has proved to perfectly describe the complex interaction between polymers and penetrants at different operative conditions, with a limited number of pure components physical parameters. Gas sorption isotherms at both cryogenic and ambient conditions can be consistently represented within this framework, suggesting that physical absorption/dissolution - rather than surface adsorption - is the dominant mechanism in glassy polymers [44].

The objective of the present work is to explore the relationship between BET-derived parameters, FFV, and thermodynamic quantities obtained from NELF modeling for a series of high-free-volume polymers, including PIMs, ladder Tröger's base (TB) polymers [45], PTMSP [46], modified Polynorbornenes (PNB) [47] and PI [28]. Such polymers have highly rigid backbones, a linear topology, and their large free volume pockets are generated during solvent molding or directly during their synthesis, without any additional processing of polymers. The analysis is based on a direct comparison between cryogenic gas sorption data and model predictions, and addresses the applicability of BET parameters (apparent surface area) - originally developed for rigid porous solids - to the interpretation of gas uptake and transport in non-equilibrium polymeric systems, thus contributing to a consistent and physically sound thermodynamic interpretation of sorption phenomena in high-FFV glassy polymers. Indeed, the novelty of this work lies in providing, for the first time, a physical rationale for the use of cryogenic N_2 sorption isotherms to elucidate the free volume characteristics of the polymer and ultimately predict its permeability. Beyond conventional FFV-permeability relationships, the analysis is strengthened by the use of Lattice Fluid equation of state, thereby ensuring a rigorous thermodynamic framework.

2. Methods

2.1. BET & FFV

The transport of small gas molecules through dense polymers occurs following the solution-diffusion mechanism, in which the three main parameters governing the process are Permeability *P*, Diffusion coefficient *D,* and Solubility coefficient *S* [35], according to Eq. (1):

$$P = D \cdot S \quad (1)$$

The diffusion coefficient, which reflects the mobility of penetrant molecules in their transport through macromolecules, is highly affected by polymer characteristics and structure. Similarly, the solubility coefficient also varies according to the different polymer matrix and the equilibrium penetrant uptake, although its magnitude is primarily influenced by the condensability of the penetrant. One of the main factors controlling the diffusion coefficient in dense polymer matrix is the fractional free volume (FFV). The FFV arises from an inefficient packing of the polymer macromolecules during cooling fabrication process, resulting in unoccupied voids where gas molecules can diffuse [48].

The fractional free volume, FFV, is often expressed as follows:

$$FFV = \frac{\widehat{V}_f - \widehat{V}_0}{\widehat{V}_f} \quad (2)$$

Here, $\widehat{V}_f$ is the volume of the polymer, expressed as volume per unit mass, obtained from experimental measurement of the polymer density at the temperature of interest. The term $\widehat{V}_0$ is the volume per unit mass occupied by the polymer chains.

One of the most widely used relationships for the estimation of FFV is the approach proposed by Bondi (FFV_B), where the occupied volume $\widehat{V}_0$ is calculated from the van der Waals volumes ($\widehat{V}_{VdW}$) of the different groups in the polymer structure through an empirical correction factor [14].

Accordingly, Bondi free volume is defined as:

$$FFV_B = \frac{\widehat{V}_f - 1.3 \cdot \widehat{V}_{VdW}}{\widehat{V}_f} \quad (3)$$

However, when this equation is applied to a broad variety of polymers, the correlation between gas permeability and FFV_B appears to be highly scattered, likely in view of its empirical nature.

The values of FFV reported in the literature are often determined from density measurements, relying on the above correlations, or, only in a few cases, from Positron-Annihilation Lifetime Spectroscopy (PALS) [49,50].

An alternative emerging method is cryogenic gas sorption, with the analysis of the isotherms, suitable to correlate in a very qualitative way the results obtained with polymer free volume: roughly, the larger the sorption, the larger the free volume. Such method is now widely employed for many membrane materials, and it will be the focus of the present work.

The technique makes use of nitrogen gas at 77 K as inert sorbate. The polymer samples were exposed to nitrogen under controlled pressure conditions, and the amount of gas adsorbed at each relative pressure point was recorded.

The resulting sorption isotherm was analyzed using the Brunauer-Emmett-Teller (BET) equation, applied to its linear region (Fig. 1), to evaluate the specific surface area (S_{BET}) of the samples [34]. This parameter quantifies the total surface area available for adsorption and, consequently, for potential interaction with penetrant molecules. The experimental procedure and data analysis were carried out following standard BET protocols, as described in detail in the Supplementary Information.

Although the BET approach is commonly applied to high-free-volume glassy polymers, its validity in such systems remains debatable. Nitrogen sorption in polymers is predominantly governed by absorption within the bulk matrix (physical dissolution) rather than by true surface adsorption, making the concept of an "adsorptive surface" somewhat ambiguous and lacking of physical meaning. Consequently, the BET-derived surface area should be interpreted as an indirect measure of the polymer accessible free volume rather than a conventional surface area in the sense of porous solids. Within this framework, only

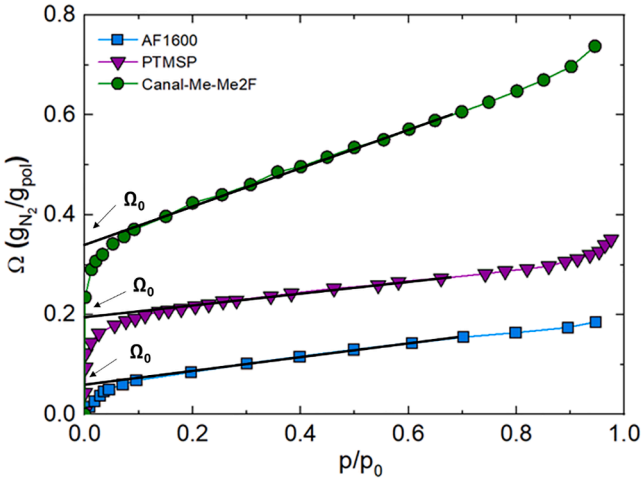

Fig. 1. Example of nitrogen sorption at 77 K, highlighting the determination of Ω_0 as the y-intercept of the sorption curve used for FFV_{77K} c; experimental data from [27,28].

the fraction of nitrogen uptake occurring prior to polymer swelling (Ω_0), thus not associated with significant structural rearrangements, is considered relevant for the determination of the free volume. In this low-pressure regime, nitrogen molecules are assumed to progressively occupy the free space between the polymeric chain through a dissolution mechanism. Penetrant molecules, when solubilized in the polymer matrix are in a condensed phase, so it is reasonable to assume a partial molar volume essentially equal to that of saturated liquid nitrogen at atmospheric pressure.

Under these assumptions and provided that a reliable estimate of the solute molar volume in the condensed state is available, the fractional free volume (FFV_{77K}) of the polymer can thus be derived at constant concentration (c_0 or Ω_0), as reported in Eq. (4):

$$FFV_{77K} = c_0 \frac{MW_{N_2} \cdot \rho_{pol}}{22414 \cdot \rho_{N_2\ (77K)}} = \Omega_0 \frac{\rho_{pol}}{\rho_{N_2\ (77K)}} \quad (4)$$

Where $\rho_{N2\ (77K)}$ is the nitrogen density at 77 K, MW_{N_2} is the molecular weight of N_2, ρ_{pol} is the density of the polymer at 77 K, and Ω_0 (in g_{N2}/g_{pol}, or c_0 in cm^3_{STP}/g) is the initial concentration of N_2 dissolved in the polymer, calculated at $y = 0$, corresponding to the initial low-pressure, isovolumetric filling of the polymer free volume by nitrogen, prior to sorption-induced polymer expansion. Finally, 22,414, expressed in cm^3_{STP}/mol, is introduced to adjust the concentration (c_0) into consistent volumetric units, yielding a dimensionless FFV.

At low temperatures, deviations from equilibrium - namely, the excess free volume trapped within the polymer matrix - are significantly larger than those at ambient conditions. The height of the characteristic "knee" in the nitrogen cryogenic isotherm corresponds to the number of moles that can be uptaken under constant-volume conditions, before any appreciable swelling occurs. This uptake reflects the amount of free volume accessible to N_2 at 77 K, providing a useful indirect probe of the polymer structure (Fig. 1).

2.2. Model description

Cryogenic nitrogen solubility was analyzed within the framework of Non-Equilibrium Thermodynamics, specifically through the non-equilibrium lattice fluid (NELF) model [39], which extends the Sanchez-Lacombe equation of state to non-equilibrium conditions, while preserving its conceptual simplicity. In this thermodynamic description, both penetrants and polymers are characterized by three characteristic parameters: temperature (T^*), pressure (p^*), and density (ρ^*). These parameters can be determined from pressure-volume-temperature

measurements (pVT) or, when such data are not available, they can be assessed with different modeling approaches: from molecular dynamics direct predictions, see e.g. Fermeglia and coauthors [51,52], or from the simulation of pVT experimental data, as illustrated by Ricci et al. [53]. Alternatively, one can also use binary solubility data in the limit of infinite dilution to calculate the polymer triplet [54,55], as carried out in the present work:

$$T^* = \frac{\varepsilon^*}{k_b} \tag{5}$$

$$p^* = \frac{\varepsilon^*}{v^*} \tag{6}$$

$$\rho^* = \frac{M}{r v^*} \tag{7}$$

As for any equation of state, phase equilibrium between the polymer and the gas phase must be satisfied. However, glassy polymers are intrinsically non-equilibrium systems, and their thermodynamic state can only be defined by introducing an additional state variable, namely the polymer mass density. In this regard, the non-equilibrium density of the polymer can be estimated by assuming a linear dilation with respect to the partial pressure of the penetrant, where the proportionality constant is the swelling coefficient k_{sw}.

$$\mu_i^{NE(pol)}\left(T, p, \omega_i, \rho_{pol}^{NE}\right) = \mu_i^{EQ(gas)}(T, p, \omega_i) \tag{8}$$

$$\frac{1}{\rho_{pol}^{NE}} = \frac{1}{\rho_{pol}^{0}}\ (1 + k_{sw} p) \tag{9}$$

Penetrant-polymer systems are modeled by applying the same mixing rules as the Sanchez Lacombe lattice fluid theory, relying on a binary interaction parameter k_{ij} for each penetrant-polymer pair. Both the swelling coefficient and binary interaction coefficient may be estimated from the analysis of gas sorption isotherms. See the Supplementary Information (SI) section for more details.

In parallel with the interpretation of sorption isotherms, the polymer free volume can also be estimated within the same Lattice Fluid theory framework. The total volume of the polymer is described as the sum of a fraction occupied by the polymer chains and inaccessible to penetrant molecules, corresponding to the characteristic volume ($1/\rho^*$); and an unoccupied fraction, which represents the free volume. The unoccupied fraction can be evaluated as the difference between the polymer specific volume and the occupied fraction. Accordingly, following the approach proposed by Costa and Storti [12], the free volume fraction (FFV_{LF}) can be calculated as follows:

$$FFV_{LF} = \frac{\frac{1}{\rho} - \frac{1}{\rho^*}}{\frac{1}{\rho}} \tag{10}$$

3. Results

Fig. 2 illustrates the correlation between nitrogen permeability and the BET specific surface area (S_{BET}) estimated from N_2 sorption data at 77 K for a broad set of polymer families, including PIMs [5,65–69], PIs [70–75] TBs [28,70,76,77] CANALs [78–82], PNBs [33,83,84], and conventional materials - i.e. PVC, PMMA, PPO, PMP, PS, PSF etc., [26, 29–32,85], as well as highly permeable glassy polymers (HP-GP) such as PTMSP, AF1600 and AF2400 [46,58].

Although dense polymers do not possess a well-defined internal surface area in the same sense as porous solids, the BET metric is often applied to the analysis of N_2 adsorption isotherms and used to correlate the free-volume-related characteristics of the polymer. Indeed, the value of apparent surface area, S_{BET}, is often used as a qualitative descriptor of the accessible FV structure within the polymer matrix (Fig. 3a).

Despite the known limitations of the BET theory when applied to dense, non-porous polymers, Fig. 2 clearly indicates a general trend

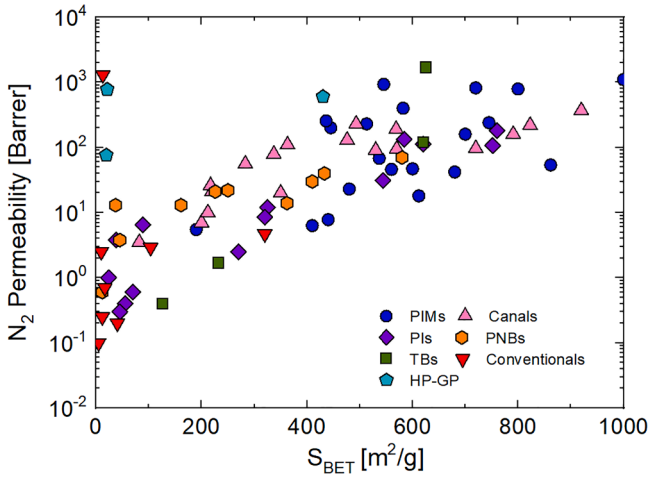

Fig. 2. Nitrogen permeability behavior with polymer (apparent) BET surface area, calculated from N_2 sorption experiments at 77 K [28,58,73,78,81,86–98].

across all polymer classes: materials exhibiting higher BET-derived surface areas tend to show proportionally higher N_2 permeabilities. In particular, the data follow an exponential trend that can be described empirically as: $P_{N_2} = A\exp(B \cdot S_{BET})$, where A and B are fitting parameters. This qualitative relationship is consistent with the idea that larger FFV - reflected here by larger apparent S_{BET} values - facilitates gas diffusion and enhances overall permeation. The observed exponential dependence resembles the well-established relationship between gas permeability and fractional free volume (FFV). However, it is important to emphasize that S_{BET} and FFV are not physically equivalent quantities: while FFV is an intrinsic property of the molecular packing and chain architecture of the polymer, S_{BET} cannot be interpreted as a rigorous structural parameter for dense polymers as it does not represent a true geometric surface area in the classical porous-material sense. Therefore, the systematic correlation of S_{BET} with gas permeability suggests that it may serve as a practical empirical descriptor for comparing relative free-volume characteristics within a given family of materials. The physical implication is not that permeability is governed by surface area, but that higher apparent S_{BET} values may serve as effective proxies for comparing polymer matrix with greater free-volume accessibility, which facilitates gas diffusion and enhances overall permeation.

In this concern, the FFV_{77K} of different dense polymers has been calculated starting from solubility data of N_2 at 77 K retrieved from the literature. Fig. 3a reports the N_2 permeability trend as a function of the initial concentration Ω_0, while Fig. 3b refers to N_2 permeability as a function of the FFV_{77K}, relying on Eq. (4).

Interestingly, it is evident that a correlation exists between the gas permeabilities, FFV_{77K}, and the concentration of sorbate in the polymer at the knee of the sorption isotherm (Ω_0). Such relationship is exponential, similar to the trend observed for the surface area obtained using the BET method (Fig. 2), although this is only a qualitative parameter for dense polymers, yet without physical meaning. In particular, PIMs and CANALs are the two classes of materials that present higher permeability and sorption capacities, as well as larger surface area. Polymers with intrinsic microporosity contain a partially ladder aromatic polyether with rigid, non-rotatable backbones that own, simultaneously, large FFV_{77K} (24–26 % as calculated from Eq.4) and effective surface area above 400 m^2/g, reflected on their large gas permeability [5,96, 99–101]. Similar considerations apply to CANALs, which also exhibit a highly rigid backbone resulting from the catalytic arene-norbornene annulation reaction [102]. However, by incorporating different end groups, side chains, or conventional C—C bonds, these materials become highly versatile [103]. Consequently, variations in chain packing led to S_{BET} values ranging from about 200 to 850 m^2/g, and FFV_{77K} values from roughly 0.1 to 0.5 (calculated by Eq. (4)) [28]. Polynorbornenes (PNBs),

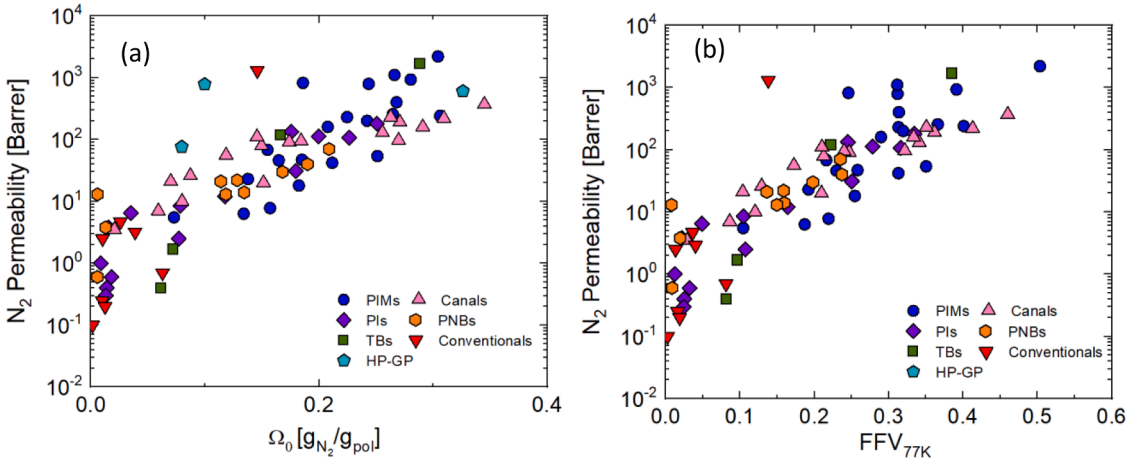

Fig. 3. Correlation between (a) gas concentration (Ω_0) from N_2 sorption at 77 K (exp. data from [5,26,33,66–68,70,72,73,77–81,83–85,96,101,108,110]), and nitrogen permeability at room temperature (exp. data from [28,57,58,73,78,81,86–98,105–107]); (b) Nitrogen permeability and the fractional free volume FFV_{77K} (calculated from N_2 sorption isotherm at 77 K as in Eq.4), in different classes of polymers.

on the other hand, have a microporous structure which reflects on high S_{BET} and FFV_{77K}, although their rigid ring.backbones provides a loose packing of polymer chains that reduces the gas sorption (0.25 to 0.12 g_{N2}/g_{pol}) and permeation (around 10 Barrer for nitrogen) with respect to PIMs [84,104].

Finally, except for a few cases, PIs, TBs and conventional glassy dense polymers are those presenting lower FFV_{77K} and surface area. Polyimides contain rigid imide rings that reduce gas permeability and, due to the presence of polar imide groups, they generally exhibit small specific surface areas [72–75]. Troger-base materials have a flexible methylene bridge in the backbone that leads to a smaller specific surface area and lower gas permeability (between 0.1 to 50 Barrer) [18,66]. Nevertheless, while free volume remains a relevant concept also for dense, non-porous polymers, S_{BET} does not directly convey intrinsic structural information in such systems. Indeed, in this context, the estimation of fractional free volume (FFV_{77K}) from nitrogen sorption data provides a more physically meaningful descriptor of the polymer packing chains than the BET specific surface area (S_{BET}).

The highly permeable glassy polymers (AF1600, AF2400 and PTMSP) as well as the conventional polymers included in the dataset (PP, PS, PVC, PMP, PSF, Matrimid, PPO, and PMMA) follow the same general permeability/FFV_{77K} and permeability/surface-area trends observed for the other polymer families. Although these materials are not typically characterized by a high free volume, the application of BET analysis to their cryogenic N_2-sorption isotherms provides qualitative insights into their free-volume characteristics.

Polymers like PTMSP [46,86], possessing a highly flexible backbone and exceptionally large intrinsic free volume, occupy the upper region of both plots, reflecting their high N_2 permeability (around 3200/3600 Barrer) and comparatively elevated apparent surface area (600–700 m^2/g). In contrast, more dense packed polymers such as PP, PS [31], PVC [32,109], PSF [29], PPO, Matrimid and PMMA [30,111] cluster toward the lower end of the distributions, consistent with their limited fractional free volume (FFV_{77K} = 0.04, 0.07, 003, 0.02, 0.04, 0.02 and 0.05, respectively) as calculated from Eq. (4), and correspondingly reduced gas permeabilities.

The alignment of conventional polymers along the same exponential trend lines as high-performance materials (e.g., PIMs, CANALs, TBs) demonstrates that the results of cryogenic N_2 sorption and also BET-derived parameters, though not meaningful for dense systems, still capture relevant variations in free-volume accessibility. In particular, the low S_{BET} and FFV_{77K} values obtained for PS, PSF, PP, PVC , and PMMA correlate well with their tight molecular packing and low segmental mobility, which restricts the formation of accessible volumes and thus limit gas transport. Conversely, PTMSP, as well as AF1600 and AF2400 - often considered the benchmark for high-free-volume commercial polymer - exhibits a significantly larger FFV_{77K}, consistent with its position as an outlier in permeability.

By extending the analysis beyond N_2 to the permeability of other gases (Fig. 4), such as CO_2, CH_4, O_2, and H_2, and considering the full set of polymers investigated, including both high-free-volume materials and conventional glassy polymers, a universal trend emerges. When plotted against the fractional free volume (FFV_{77K}), the permeability of all these gases follows the same semi-empirical correlation:

$$P_i = A_i \, exp^{B_i \cdot FFV_{77K}} \tag{11}$$

where A and B are fitting parameters specific to each gas *i*. This exponential relationship between a transport property, Permeability, and the FFV_{77K} is a classical outcome of the free-volume theory in its simplest formulation. The expression, similar to the correlation derived for N_2 permeability and S_{BET} even though they do not have the same physiscal meaning, comes from the analysis of penetrant diffusivity, which employs an extensive database encompassing a large variety of glassy polymers, that lead to the same formal correlation for D, where is found to be a linear function of 1/FFV, commonly expressed as ($D = A \, exp \, (-B/FFV)$ [94]. This analogy observed between the permeability (Eq. (11)) and the established diffusivity correlation stems from the solution-diffusion mechanism governing gas transport in polymers. Since permeability can be expressed as Eq. (1), and the fractional free volume is expected to have a limited effect on solubility while exerting a much stronger influence on diffusivity - as typically observed in glassy polymers - the diffusivity correlation can be reasonably extended to permeability, neglecting secondary variations in solubility.

The observed exponential trend indicates that the FFV_{77K}, evaluated with the methodology presented in this work, represents a physically meaningful descriptor of gas transport: an increase of FFV_{77K} reflects the enhancement of chain accessibility and connectivity across all the materials considered, thus resulting in systematically higher permeabilities. The observed correlations yield clear and consistent trends for all examined gases, demonstrating that FFV_{77K} constitutes a robust parameter for rationalizing permeability data over a broad range of polymer systems. Nevertheless, given the wide range of polymer types, a considerable and systematic degree of scattering is observed, highlighting the complex relationship between P and FFV_{77K}. Notably, the present FFV-based description offers a more reliable representation of gas transport behavior than correlations based solely on accessible surface area, which lacks a clear physical definition in dense polymeric materials.

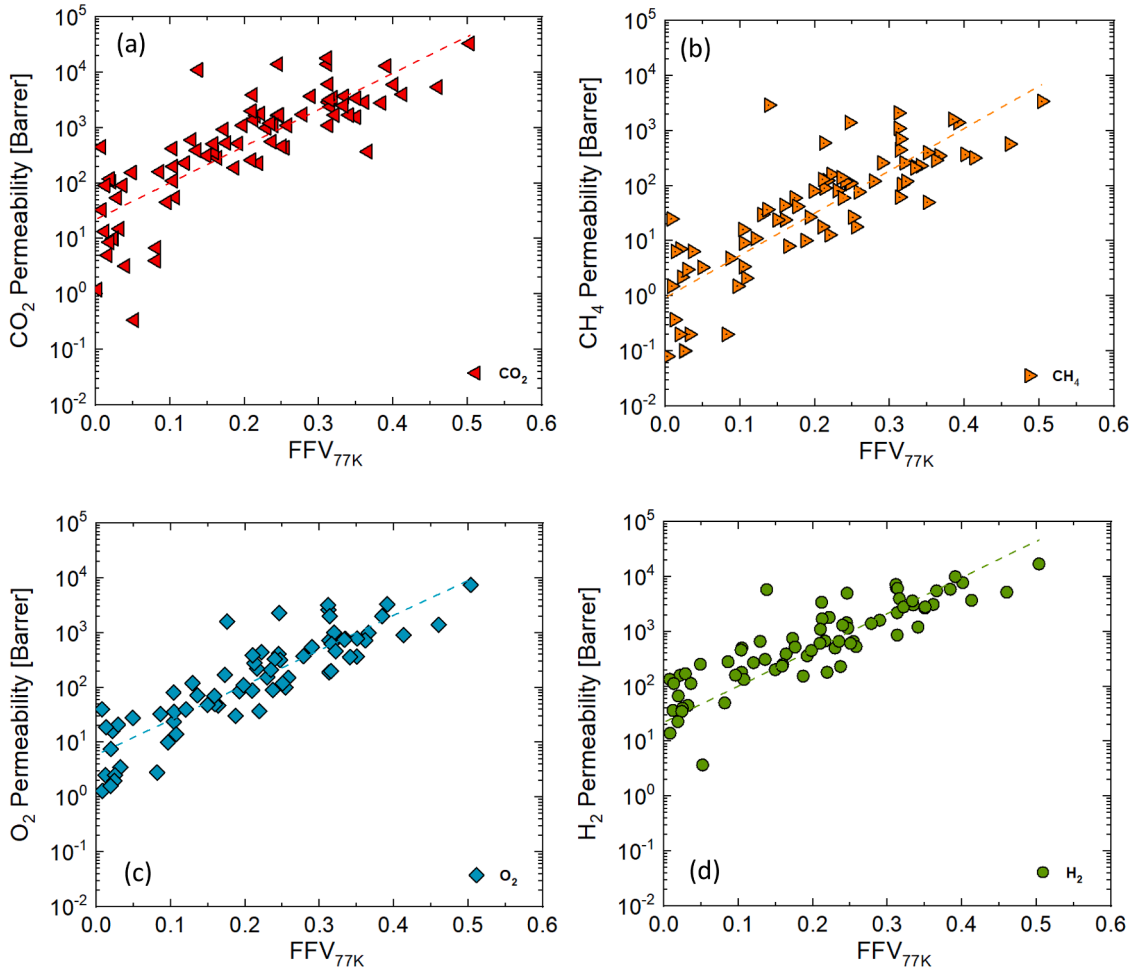

Fig. 4. Gas permeability plot versus FFV_{77K} (calculated from N_2 sorption isotherms as in Eq.4) obtained from cryogenic sorption experiments for (a) CO_2, (b) CH_4, (c) O_2 and (d) H_2, in various polymers [28,58,73,78,81,86–98,105–107].

An alternative mean to the evaluation of the polymer free volume is represented by the use of a EoS approach; in particular, in the framework of a Lattice Fluid model, the characteristic density of the polymer represents the close-packed configuration, allowing thus to calculate FFV_{SL}, according to Eq. (10): Fig. 5 compares the values calculated from Sanchez-Lacombe EoS and those determined from cryogenic N_2 sorption (FFV_{77K}).

The Lattice Fluid model by Sanchez and Lacombe [55,112], in its non-equilibrium version (NELF) [39,63], is well known for its ability to describe the solubility of gas and liquid penetrants in glassy polymers [38,40,43,113], even in cryogenic conditions [25,26]. Therefore, a consistent interpretation of experimental data is obtained by considering penetrant dissolution in a uniform and dense phase (the glassy polymer), undergoing volume swelling with nitrogen as penetrant. The N_2 sorption data can be properly described by using the NELF model, able to provide a deeper understanding of results obtained, clarifying the physical meaning of the operating parameters and how they relate to the polymer-penetrant interactions. Table 1

The calculation of gas uptake at various pressures at constant temperature relies on the pressure behavior of the non-equilibrium polymer density (ρ_{pol}^{NE}), often described by a linear trend (two main parameters are thus considered: pure polymer density (ρ_{pol}^{0}), and the swelling coefficient (k_{sw})), as well as binary interaction coefficient (k_{ij}) (see Table 2).

The density is estimated by taking its experimental value at 293 K and accounting for temperature effects using available pVT data [114] or, when such data are not available, by applying a thermal expansion coefficient of $1{\cdot}10^{-4}$ K^{-1}, which represents an average value for glassy

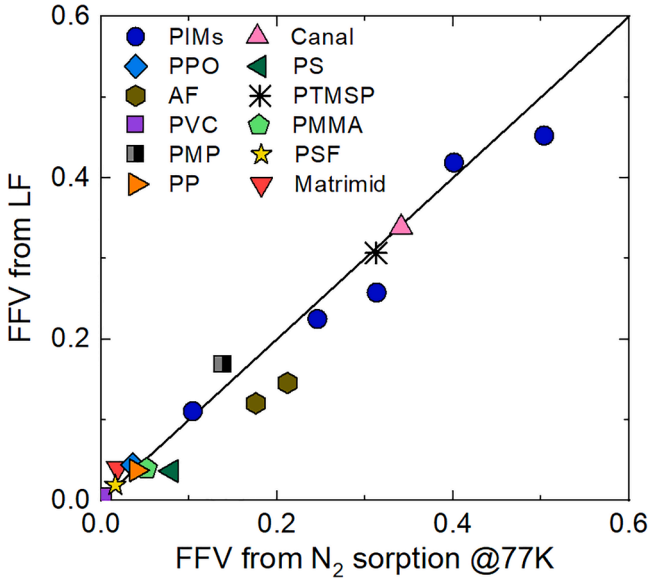

Fig. 5. Parity plot of FFV calculated from cryogenic N_2 sorption isotherms at 77 K (FFV_{77K}) versus FFV calculated from LF-EoS (FFV_{SL}).

polymer phases. The binary interaction coefficient k_{ij} determines the initial slope of the isotherm, and it controls the sorption behavior in the

Table 1
Characteristic parameters of the LF/NELF model for the pure penetrants and polymers considered in this work.

Polymer/ Penetrant	T*	p*	ρ*	Reference
PIM-1	872	523	1.438	[56]
PIM-7	800	400	1.5	[57]
PIM-6FDA-OH	850	500	1.46	This work, from binary solubility data*
PIM-EA-TB	825	600	1.8	This work, from binary solubility data*
PIM-TMN-Trip	750	600	1.53	This work, from binary solubility data*
AF1600	575	280	2.16	[58]
AF2400	624	250	2.13	[58]
Matrimid	880	450	1.32	[59]
PTMSP	610	380	1.125	[60]
CANAL-Me-iPr	600	400	1.5	This work, from binary solubility data*
PMP	850	270	0.96	[61]
PPO	739	479	1.177	[41]
PP	692	297.5	0.8828	[62]
PS	750	360	1.099	[41]
PSF	830	600	1.31	[63]
PVC	680	620	1.487	[64]
PMMA	695	560	1.27	[41]
N_2	140	185	0.925	[26]

* more details are reported in the Supplementary Information section.

Table 2
Binary interaction parameter k_{ij} and swelling coefficient k_{sw} for NELF EoS model.

Polymer	k_{ij}	k_{sw} [MPa^{-1}]
PIM-1	0.3	1.2
PIM-7	0.2	1.8
PIM-6FDA-OH	0.32	0.91
PIM-EA-TB	0.10	3.1
PIM-TMN-Trip	−0.2	4.0
AF1600	0.17	2.7
AF2400	0.2	3.5
Matrimid	0.54	0.25
P84	0.668	0
PTMSP	0.32	2
CANAL-Me-iPr	0.37	1.5
PMP	0.15	2.6
PPO	0.52	0.05
PP	0.25	1.7
PS	0.25	1.55
PSF	0.568	0.22
PVC	0.27	0.07
PMMA	0.15	1.45

low-pressure regime. In this region, swelling of the polymer matrix is negligible because the penetrant concentration remains very low, allowing k_{ij} to be interpreted as a measure of the purely thermodynamic affinity between nitrogen and the polymer.

At higher pressures, the isotherm shape is governed by the penetrant-induced swelling, described by the coefficient k_{sw}, which accounts for the volumetric expansion of the polymer. The value of k_{sw} is associated to the slope of the linear region of the sorption isotherm. Accordingly, the concentration at which the isotherm bends toward the x-axis, basically the location of the isotherm knee, may be associated to the isovolumetric solubility, corresponding to the amount of N_2 molecules that could be dissolved in the polymer matrix before any swelling takes place (Fig. 6). This concentration is closely related to the value Ω_0 derived from cryogenic sorption measurements, which corresponds to the maximum gas uptake prior to polymer deformation and denotes the saturation of the polymer accessible free-volume sites (Fig. 6S in SI).

As already observed by Horn [48], it is relevant to compare the FFV_{LF} calculated with our LF approach with that from Bondi's group

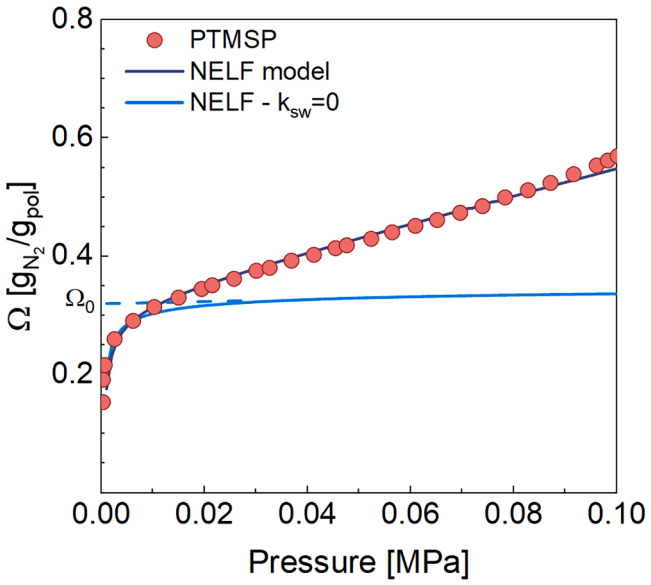

Fig. 6. Cryogenic Nitrogen sorption isotherms in glassy polymers: symbols represent literature experimental data from BET analysis at 77 K while lines are NELF model curves; experimental data from [27].

contribution, by considering the effect of V_0 versus $1/\rho^*$.

Fig. 7a shows the relationship between these two quantities, highlighting a slight deviation from the identity line, with V_0 being systematically lower than $1/\rho^*$ for the vast majority of the polymers considered. In this plot, the data points were recalculated using an empirical factor of 1.45, highlighting the shift with respect to the shaded region, which remains representative of the original Bondi estimate (V_0 calculated as $1.3 \cdot V_{VdW}$). This trend confirms that Bondi's method underestimates the actual occupied volume of the polymeric matrix. Such deviation may take place because V_0 is based on Van der Waals volumes, corrected by the empirical factor 1.3, thus representing an intrinsic molecular measure that does not capture the experimentally accessible free volume. In this context, several studies [24,36,48,115,116] have indeed pointed out that this multiplication factor is not universal and can differ from the conventional value of 1.3 originally proposed by Bondi. In fact, when the empirical correction applied to the van der Waals volume is increased from the conventional value of 1.3 to 1.45, the recalculated Bondi FFV_B aligns much more closely with the mean values obtained from the BET and EoS methods, with error bars indicating the small differences between the two approaches (Fig. 7b). The value 1.45 is empirical in nature, but it is consistent with previous observations. Jones et al. [117]. showed that, above and below T_g, the factor can be interpreted as an effective packing parameter ranging from 1.2 to 1.76, while Dlubek [118] applied the same 1.45 factor for semi-crystalline polymers at $T=T_g$. Physically, this adjustment suggests that the polymer matrix occupies more space than captured by conventional metrics, leading to a smaller calculated free volume. Consistently, in Fig. 7b the shaded region reflects the FFV_B ranges associated with Bondi's formulation, while the points are representative of the FFV values calculated using 1.45 as the empirical factor. This modification leads to a 17 % reduction in the mean absolute deviation, indicating a more consistent agreement with the experimental FFV_{77K} (all values are presented in Table 3S). The largest discrepancies are observed for high-free volume polymers, whose microstructure is strongly affected by physical aging and thermal history, making it particularly difficult to reproduce their behavior through a group-contribution approach alone.

The analysis of the N_2 sorption curve provides not only the value of gas uptake at constant volume (Ω_0), but one can also obtain useful information about the central portion of the curve, related to penetrant induced swelling. Such region can be examined to compare the

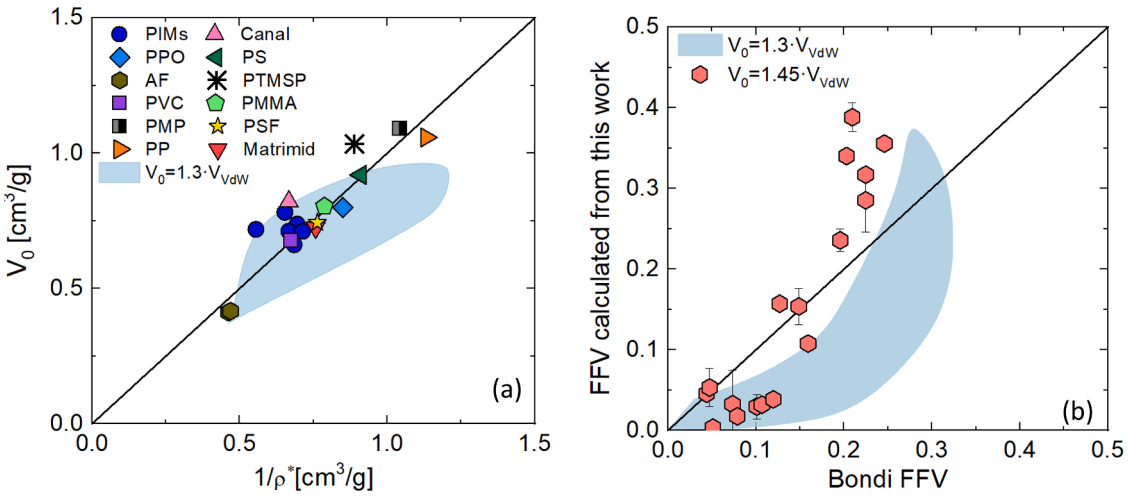

Fig. 7. (a) Relationship between 1/ ρ* of the polymer and V_0 of the polymer calculated from Bondi; (b) Comparison between Bondi FFV and the mean experimental FFV from LF EoS and N_2 sorption from BET at 77 K, with error bars indicating differences between the two methods.

behaviors of the sorption isotherms at 77 K for the different polymers, evaluating the swelling coefficient if employing the NELF model, or, in a more empirical fashion, simply looking at the slope of the curve.

The dependence of transport properties on the swelling coefficient has been examined, revealing that, despite the heterogeneity of the dataset, polymers exhibiting higher swelling coefficients at 77 K often display lower CO_2/N_2 selectivity (Fig. 8a). The trend becomes clearer when considering that the swelling coefficient, which represents the sensitivity of the polymer matrix to penetrant-induced perturbations, is effectively captured by the average slope of the sorption isotherm at high activities (Fig. 8b). A steeper slope indicates a stronger polymer response to sorption, typically associated with enhanced matrix expansion, greater accessible free volume and chain rearrangement. Such swelling behavior typically reflects a looser or more open chain packing, which facilitates the permeation of larger molecules and ultimately lowers the selectivity by reducing the capacity of the polymer to discriminate between gas molecules. The observed trend can also be rationalized mechanistically: polymers with a more rigid matrix, less prone to swelling and plasticization, preserve a higher sieving capacity; in such systems, the mobility of the penetrant is much affected by its size. Therefore, the rigidity of the polymer chain improves selectivity by maintaining a narrower free volume distribution and stronger molecular discrimination [119–121].

The dispersion observed across the dataset highlights that each class of polymers responds differently to low-temperature sorption and swelling due to differences in backbone rigidity, free-volume architecture, segmental dynamics and penetrant-polymer interactions. While swellability is a material-dependent property, its correlation with gas pair selectivity across chemically and structurally diverse polymers indicates that it remains a meaningful parameter for rationalizing gas-separation performance. In this sense, the combination of N_2 cryo-sorption data and NELF thermodynamic modelling analysis provides a consistent picture of how penetrant-induced density changes modulate gas permeability and selectivity in a wide variety of polymeric materials.

4. Conclusions

This work demonstrates that cryogenic N_2-sorption measurements provide meaningful and experimentally accessible descriptors of free volume in polymeric membranes. Although dense polymers do not possess a well-defined internal surface area in the classical sense, the penetrant concentration at the knee of the isotherm (Ω_o), and the calculated FFV_{77K} consistently correlate with gas permeability across a wide range of polymer families. These parameters capture subtle

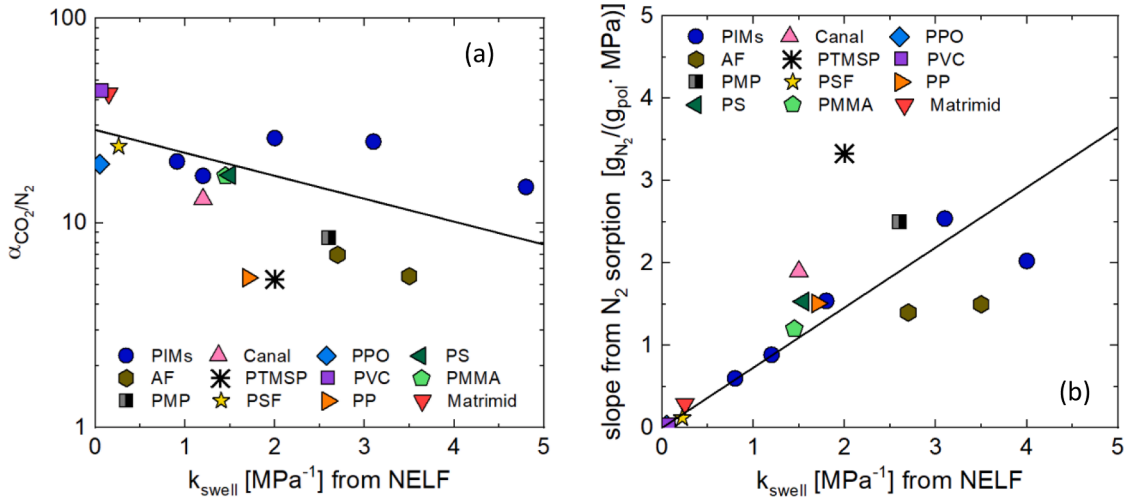

Fig. 8. (a) CO_2/N_2 selectivity at 35 °C in the investigated polymer as a function of k_{sw} obtained from NELF modeling for Nitrogen at 77 K; (b) Correlation of swelling coefficient calculated from NELF and the slope of the sorption isotherm at 77 K obtained from BET analysis.

variations in chain packing and volume accessibility that directly govern gas-transport behavior, thus offering a practical route to compare both advanced high-free-volume materials and conventional commercial polymers within a unified framework.

This experimental evidence aligns with predictions from the Non-Equilibrium Lattice Fluid (NELF) model, which offers a physically grounded bridge between sorption thermodynamics and free-volume-controlled permeability. By linking isotherm behavior to the characteristic density and polymer-penetrant interaction parameters, NELF provides an internally consistent estimate of fractional free volume (FFV_{LF}) that closely follows the trends derived from cryogenic sorption measurements. The agreement between these two independent approaches strengthens the interpretation that cryogenic sorption effectively probes the thermodynamic availability of free volume in nonequilibrium polymer matrices.

The comparison with Bondi's group-contribution method further reinforces this view. Bondi's van der Waals-based volumes consistently underestimate the actual occupied volume for many polymers, particularly those characterized by high free volume or intrinsic microporosity. This discrepancy arises because van der Waals volumes do not account for nonequilibrium structural features, or the presence of interconnected backbones that contribute to real polymer free volume.

The observed dependence of transport performance on low-temperature swelling further illustrates how free-volume accessibility, as well as segmental relaxation and penetrant-polymer interactions, affects molecular discrimination, which facilitates the transport of larger penetrants and reduces size-based discrimination. This demonstrates that cryogenic sorption isotherms are suitable tools for studying materials used in gas-separation membranes of both advanced materials and conventional polymers, even if no microporous structure is present. When interpreted without relying on the BET model, which lacks physical meaning for non-porous systems, such measurements provide an approximate yet significant indication of the accessible free volume within the polymer.

Overall, the analysis of the data presented shows that the correlations between the structural properties of the polymers and their permeability performance are both coherent and meaningful, remaining the central parameter governing gas transport in polymeric membranes. In conclusion, the methodology presented here offers a robust and versatile framework for interpreting transport phenomena in systems with diverse morphologies, for rationalizing permeability trends and for guiding the design of high-free-volume membrane materials.

CRediT authorship contribution statement

Roberta Di Carlo: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Lucia Caraceni:** Writing – review & editing, Investigation, Data curation. **Virginia Signorini:** Writing – original draft, Methodology, Investigation, Data curation. **Matteo Minelli:** Writing – review & editing, Supervision, Funding acquisition, 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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2026.114723.

Data availability

Data will be made available on request.

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