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*Gas Sorption Isotherms in Swelling Glassy Polymers - Detailed
Atomistic Simulations*

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Abstract

Detailed atomistic simulations were carried out for swelling polymer/gas systems related to experimental sorption and dilation data for CO₂ and CH₄ in three glassy polymers (polysulfone PSU, the polyimide 6FDA-TrMPD, and a polymer of intrinsic microporosity PIM-1) at 308 K (35 °C) and pressures up to 50 bar. Corresponding experiments were performed with a gravimetric sorption balance and a dilatometer based on a capacitance distance sensor. For each polymer/gas system molecular packing models were prepared and equilibrated for two reference states: the pure polymer is taken as reference for the respective “unswollen” state and similarly the state of the highest penetrant pressure reached in the corresponding experiment is taken to represent the “swollen” state. Models for the latter were constructed in agreement with experimental data (pressure, temperature, gas concentration and volume dilation). Concentration-pressure isotherms of each polymer/gas system were obtained using Grand Canonical Monte Carlo (GCMC) simulations for both reference states (depleted of gas molecules), which are in good agreement with the experimental data in the respective pressure range. As expected these isotherms – due to the simulation technique used, merely based on hole-filling in a static host matrix - do not represent the sorption behavior over a broader range of gas pressures which may involve significant structural rearrangements as well as swelling and relaxational phenomena. Nevertheless, a linear combination of the two GCMC-isotherms allows the interpolation in order to describe the nonlinear gas sorption in the glassy polymers under investigation covering the penetrant pressure range between the reference states in good agreement with the experimental results.

KEYWORDS. Gas sorption, dilation, molecular modeling, polysulfone, polyimide, polymer of intrinsic microporosity (PIM-1)

1 Introduction

The behaviour of amorphous polymers in contact with gas atmospheres is still an area of both, fundamental scientific interest and applied industrial research. Applications of gas/polymer systems range from the use as barrier materials or protective coatings to active layers in sensor applications ('artificial nose') and of course the field of gas separation membranes. In many of these applications, higher concentrations of small penetrant molecules may lead to changes of the polymer, such as swelling or plasticization. This effect is utilized in processing applications, where, e.g., supercritical carbon dioxide (CO₂) can be used as a plasticizer.¹

The phenomenon of penetrant induced plasticization of glassy polymers is also observed in gas separation membranes². The observed plasticization and the associated relaxations in the polymer matrix change its local structure and *free volume*, and thereby affect the permselectivity of the material³. The origin and mechanism of these structural relaxations are not fully understood, yet, as are the factors that influence solubility and mobility of the plasticizing penetrant. At present, this lack of knowledge still leads to development strategies for new or optimized materials, which are in part determined by trial and error. A deeper understanding of the phenomena that accompany gas sorption on the molecular level is therefore needed to control material properties and enable a targeted design of functional materials. In order to address this topic, in this work laboratory experiments are combined with detailed atomistic molecular simulations. In a previous publication we presented our approach, including also a thorough kinetic analysis of the sorption and dilation experiments as well as their interpretation in the framework of phenomenological models, using the example of carbon dioxide in polysulfone (PSU)⁴. Molecular models of selected reference states (with respect to penetrant loading and dilation) were analyzed in regard to their free volume characteristics and sorption isotherms were calculated based on Grand Canonical

Monte Carlo (GCMC) simulations. In this paper we focus on the sorption isotherms obtained based on this approach for additional glassy polymers and carbon dioxide and methane.

Molecular modeling of glassy polymers

Forcefield based Molecular Dynamics (MD) simulations are performed in femtosecond steps, but reliable results are usually not obtained until a nanosecond of net simulation time has been attained. Using periodic boundary conditions it is feasible to represent the essential behavior and properties using relatively small models of a few thousand atoms⁵. Molecular packing models of amorphous polymers may be analyzed using several established methods in order to reveal structural features on an atomistic level, such as densities and the free volume distribution⁶, or dynamic properties, such as kinetic energies or diffusivities of penetrant molecules^{7,8} from a molecular dynamics (MD) simulation run.

Limitations with respect to size of the models as well as of the simulation timescale up to several nanoseconds still constitute a significant constraint when glassy polymers exhibiting a complex structure and higher fractional free volume (FFV) are to be investigated. However, just these features often have to be regarded as a prerequisite for materials with potential as high performance materials with good permselectivities for membrane separation applications. This is even more true when dilation and plasticization phenomena affect the penetrant sorption and transport in the polymeric matrix which is often the case at higher concentration levels of penetrants strongly interacting with the polymer.

Initiated by membrane applications, several investigations took place in the field of gas sorption in glassy polymers that utilize detailed atomistic molecular simulation techniques. The basic simulation techniques related to materials science of polymeric membranes are well documented in⁹.

For the calculation of solubilities of small penetrants in dilute solutions, the Widom method¹⁰ has been implemented for glassy polymers by Gusev and Suter^{11,12}. A more generalized direct-particle-deletion scheme for the investigation of larger penetrants at higher concentrations has been developed by Siegert et al.¹³ on the basis of an algorithm applicable to model systems by Boulougouris et al.¹⁴. Cozmuta et al.¹⁵ investigated solubilities of several polymer/gas systems using a combined MD and GCMC simulation method to calculate the Henry's constant (see eq. 3). Wang et al.¹⁶ recently presented a study of diffusion and solubility in the high free volume polymer PTMSP, linking the temperature dependency of the permeability to that of the distribution of cavity sizes, with reasonable agreement to experiments. Latterly, Eslami and Müller-Plathe¹⁷ describe a novel computational method¹⁸ to calculate solubilities of several gases in polystyrene over a wide range of temperatures and pressures. With a combination of calculated excess chemical potentials and partial molar volumes, both by utilizing the Widom test particle insertion method, they predicted sorption isotherms for several gases in polystyrene which are in good agreement to experimental data.

As mentioned above, some methods already exist to predict gas transport properties of polymers from simulations. Often well agreeing results were obtained for ideal circumstances – small penetrant gases, rubbery polymers and low penetrant concentrations; they frequently failed when applied to less moderate conditions – e.g., high penetrant concentrations, long time scales, large penetrants or glassy polymers with complex structure.

The time scale of MD simulations is limited to a few nanoseconds and therefore it is not possible to directly simulate relaxations of the glassy matrix as they are observed experimentally. Experiments, on the other hand, yield results of the real macroscopic system, and though molecular details cannot be observed individually, the accumulated effects permit the analysis through models on a statistical or phenomenological basis.

The aforementioned gas induced plasticization of polymers presents such a case where the gap of time scales between experiment and available simulation time amounts to several orders of magnitude.

As in previous work^{4,19,20,21} we pursue a new approach of a combined analysis of experimental and modeling results in order to establish, where possible, a convergence of boundary conditions or, alternatively, identify and isolate comparable aspects of these seemingly incompatible methods. This work concentrates on the investigation of sorption isotherms measured experimentally and their comparison to simulated sorption isotherms utilizing the models of two reference states built from experimental input.

The investigated polymer/gas systems were selected with respect to application aspects of gas separation. The permeation of gaseous penetrants through polymeric membranes is a rather complex process, involving a gas mixture and a steady-state concentration gradient through the membrane. Properties of the membrane material and its changes as well as transport properties of the gases are therefore not easily attributed to individual phenomena. The fundamental processes of penetrant sorption, transport (diffusion) and relaxation of the matrix underlying the gas separation are, with regard to the combined analysis of experiment, phenomenology and simulation, better investigated utilizing sorption and dilation isotherms of single gases. Here, the step by step procedure of increasing the pressure allows a thorough kinetic analysis and the determination of (quasi-) equilibrium conditions.

Six polymer/gas systems were selected for investigation in this work. CO₂ and CH₄ were selected as penetrant gases because of their vital roles in industrial applications and because of their differing molar, thermodynamic and plasticization properties. Polysulfone (PSU) is a widely investigated conventional glassy polymer with regard to CO₂ sorption^{22,23,24,25,26,27,28}

and can therefore be used to validate the experimental procedures used in this work. Polymers of the class of 6FDA-polyimides, generally exhibiting a larger *free volume* than PSU, are known to show excellent transport and solubility characteristics with respect to gas separation applications. They furthermore tend to be susceptible to plasticization²⁹, making the 6FDA-TrMPD (PI4) an ideal choice for the desired investigations. Different *free volume* characteristics may be expected to be present in *polymers of intrinsic microporosity* (PIMs). This new class of polymers, with structures of varying degree of order, shows promising features which have yet to be fully investigated^{30,31,32,33}, especially with respect to gas sorption properties. For this study the amorphous, membrane forming polymer PIM-1 was selected³⁴. It has to be noted that for this polymer different states depending on the sample preparation and history have been identified³⁵, cf. our preparation described in section 2.1.1. In contrast to other simulation studies addressing membrane properties (e.g. for PIM-1^{36,37}), we attempt to describe the sorption behaviour over a wide range of pressures up to 50 bar taking into account the swelling induced by the penetrant molecules.

2 Experimental

2.1 Materials

2.1.1 Sample Preparation

Commercial poly(sulfone) (Ultrason S) was obtained from BASF AG, Germany, as a melt extruded film of 100 μm thickness. DSC-measurements at 10 K/min showed non-crystallinity and a glass transition at $T_g=190^\circ\text{C}$. Measurements in a density-gradient column yielded a density of $\rho = 1.24 \text{ g/cm}^3$.

The polyimide 6FDA-TrMPD (PI4) was synthesized³⁸ at GKSS Research Centre*. Films were obtained from the resulting flakes by dissolving in dichloromethane and spreading onto a glass plate by a coating knife. After slow solvent evaporation in a chamber of decreasing solvent vapor atmosphere, the films were shortly immersed in water to detach from the glass plate and then vacuum dried at 150°C , resulting in dry films of 120 μm thickness. The glass transition temperature was determined to be $T_g=380^\circ\text{C}$ (DSC, 10K/min) and a density of $\rho=1.352 \text{ g/cm}^3$ was found (density gradient column, aqueous $\text{Ca}(\text{NO}_3)_2$ solution).

The polymer of intrinsic microporosity^{39,40} PIM-1 was also synthesized at GKSS Research Centre*⁴¹. The yellow powder was dissolved in chloroform and cast into a Petri dish inside a chamber of decreasing chloroform vapor atmosphere. Immediately after detaching the films in water, they were immersed in ethanol for 8 hours to reduce the water content and then vacuum dried at 150°C for 12h. The transparent film of yellow color had a thickness of $d=150 \mu\text{m}$ and a density of $\rho=1.124 \text{ g/cm}^3$. PIM-1 does not show a glass transition below the degradation temperature of $T_{\text{deg}}\approx 350^\circ\text{C}$.

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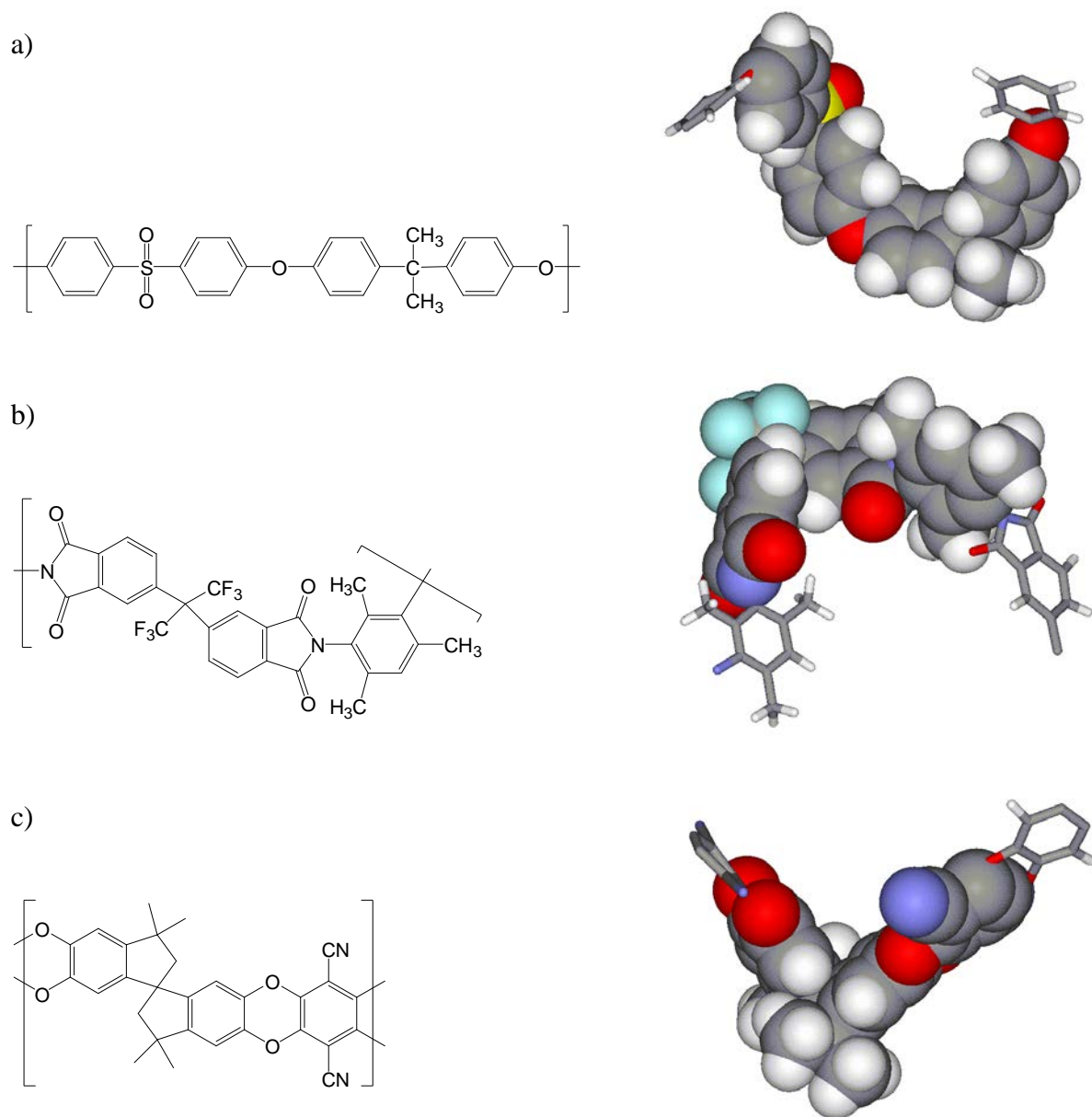


Figure 1. a) Chemical structure of poly(sulfone) (PSU), b) 6FDA-TrMPD polyimide (PI4) and c) PIM-1. In the corresponding equilibrated models of a single repeat unit (right), atoms are represented by spheres of van der Waals radii: Sulfur (S): yellow; Oxygen (O): red; Carbon (C): grey; Hydrogen (H): white; Nitrogen (N): purple; Fluorine (F): light blue.

The chemical structures of all three polymers are depicted in figure 1 along with a 3D-representation of the monomers by the van der Waals radii of the atoms.

2.1.2 Gases

Carbon dioxide (CO₂) and methane (CH₄) of purity >99.5 % were used as received from Air Liquide Deutschland GmbH.

2.2 Sorption and dilation measurements

Gravimetric sorption measurements were carried out using an electronic microbalance Sartorius M25D-P of Sartorius GmbH (Göttingen, Germany) which is situated in a pressure cell designed to bear pressures well over 50 bar. The film sample of uniform thickness was cut into several pieces (~10x10x0.1 mm) and put onto the balance pan inside the cell, which is then evacuated at $p < 10^{-5}$ mbar until any significant weight change has ceased. After degassing of the sample, the gas-pressure (CO₂ or CH₄) is increased in a series of stepwise increments and the weight gain Δm of the sample is observed for at least 24 hours at each step. As the effect of buoyancy is nearly instantaneous, compared to the slower kinetics of the weight gain due to sorption, it is easily eliminated from the data. The weight gain is converted into the commonly used units of cm³(STP)/cm³(polymer) using

$$C = \frac{\hat{V}_{id} \Delta m}{\hat{M}_{CO_2}} \cdot \frac{\rho_0}{m_0} \quad (1)$$

where \hat{V}_{id} is the volume of a an ideal gas at standard conditions (STP), \hat{M}_{CO_2} the molar mass of CO₂ and ρ_0 and m_0 the density and mass of the polymer prior to any measurement.

Gas induced swelling of the sample is determined in a similar pressure cell containing a gas pressure dilatometer. Here, the length l of a sample strip is monitored by a capacitance distance sensor, and its change Δl is converted to the volume change ΔV using

$$\Delta V / V_0 = (1 + \Delta l / l_0)^3 - 1 \quad (2)$$

assuming isotropic swelling (index 0 denotes initial values). The gas pressure was increased simultaneously to the sorption measurements in the same steps, to ensure the deduction of a proper concentration-dilation relationship.

The temperature of both, the sorption and the dilation the setup, was held constant by an air-bath at $35^{\circ}\pm 0.1^{\circ}\text{C}$. A more thorough description of the setups can be found in previous publications^{4,21,28,42}.

3 Atomistic simulations

3.1 Modelling details

For the molecular simulations described in this work software packages of Accelrys, Inc. (San Diego, CA), in combination with own analysis programs were used. Amorphous polymer packings were constructed using the Theodorou/Suter method^{43,44} as implemented in the *Amorphous_Cell* module of *InsightII* and *Materials Studio*⁴⁵. For all three investigated polymers, the specific simulation approach to obtain a respective atomistic packing model has been described in previous articles; for PSU¹⁹ and PI4²⁰ the MD simulations were performed with the Discover engine using the *COMPASS* forcefield, for PIM⁴⁶ the PCFF forcefield has been applied. Grand canonical Monte Carlo (GCMC) simulations of sorption isotherms were realized with the *Solid_Sorption* module of *Cerius2*. Calculations for the packing model preparation and the GCMC simulations were performed on SGI Octane workstations while the longer MD simulations and all analyses of trajectory files were carried out using (max. 8) Opteron cores at a node of a Linux cluster.

3.2 Packing models

Based on experimentally obtained (swelling) parameters, atomistic packing models for every polymer have been built at 308 K (35 °C) for three “states”: (i) the pure polymer under a bulk pressure of 1 bar called the “nonswollen” state, and the two respective “swollen” states at the

highest experimental gas pressure for (ii) the polymer/CO₂ system, and (iii) the polymer/CH₄ system. The basic procedure of gaining feasible packing models of both, the “nonswollen” and the “swollen” state has been described in detail in previous publications, e.g., for the polysulfone model *PSU* and the CO₂-swollen model *PSU80*^{4,19}, and will only shortly be recapitulated here: In that case, at first, a polymer chain is grown in a cubic simulation cell containing a large number of obstacles (~400 CO₂ molecules) to prevent packing artefacts (e.g. ring catenations or spearing) under periodic boundary conditions. The original size of the cell is chosen such that the resulting density is at about 10% of the desired target density (see Table 1). The obstacles are then removed until their number matches the concentration of the swollen state and in the case of methane sorption are replaced by the CH₄ molecule. Following the density adjustment, a series of NVT- and later NpT-MD-runs was performed to equilibrate the model, i.e., until the density of the model was stable within normal volume fluctuations and reasonably close to the target density, resulting in the swollen reference state.

The packing models for the “swollen” states are named *POLxx*, where *POL* stands for the three polymers (*PSU*, *PI*, *PIM*) and *xx* for the number of penetrants needed to match the experimental concentration at the reference pressure (see Table 1). Packing models of *PSU80* and *PI4* have been presented in refs.⁴ and ²⁰. A packing model of the CO₂-swollen state of PIM-1, containing 206 CO₂ molecules (*PIM206*) is shown in Figure 2.

At the upper right side of Figure 2a, the characteristic polymer structure of PIM-1 can be nicely seen: rigid ladder elements consisting of three ether bridged phenyl rings between sites of contortion (spiro-centres).

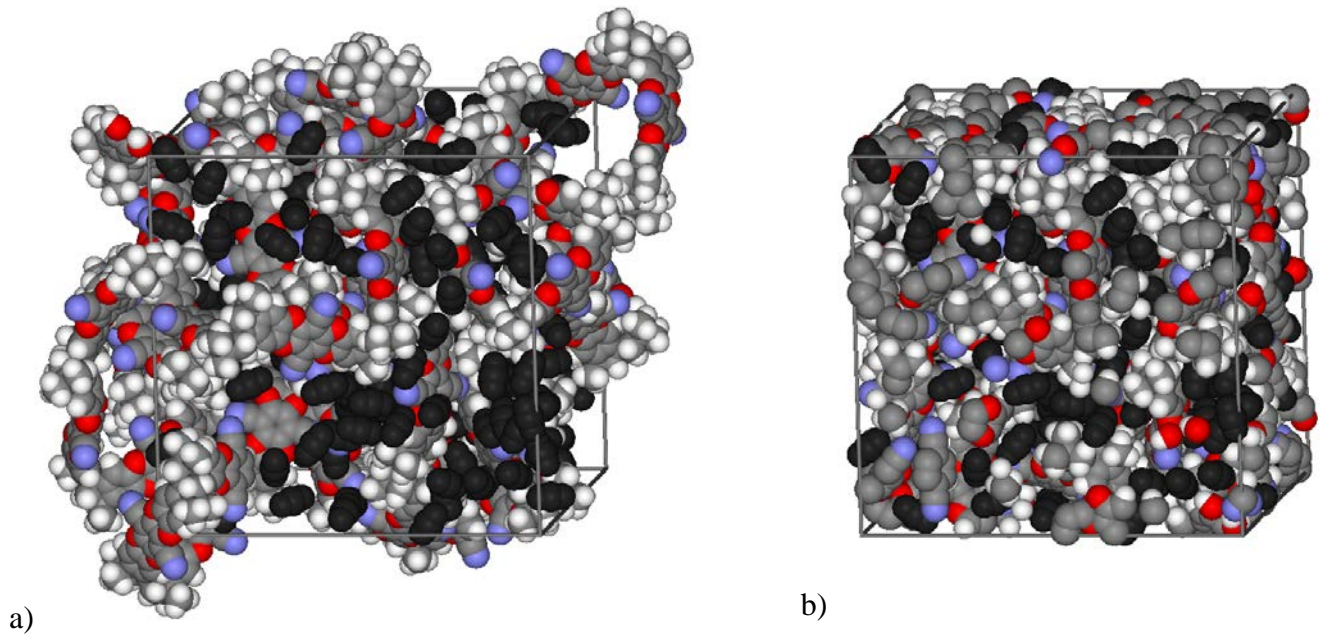


Figure 2. Single packing model for swollen PIM-1 at 50 bar CO₂-pressure and 308 K (PIM206) in its representation as five molecule chains containing 15 monomer units (each) as depicted in Figure 1c (a) and as one simulation cell with three-dimensional periodic boundary conditions (3D-PBC) applied (b). Edge length of the simulation cell is 38.6 Å; The color code is: grey (C), white (H), red (O), blue (N), CO₂ is displayed as a triatomic molecule in black.

It should be noted that due to the rigidity of the monomer, PIM-1 models were packed using 5 separate chains in contrast to PSU and PI4 models, where only one chain was needed for the specified number of repeat units. By removing the penetrant molecules, models are derived of the polymer *matrix* only, indicated by the index *m* (e.g. *PSU80m*), which were used to perform the GCMC-simulations on the penetrant-swollen polymers to calculate respective sorption isotherms.

For the “nonswollen” state of the polymers, these models were taken and after another density adjustment the equilibration procedure was repeated, thus resulting in the models *PSU*, *PI4* and *PIM*.[†]

[†] Note that PI4 denotes the „empty“ packing model of PI4 while PI76 and PI156 represent models loaded with CH₄ and CO₂, respectively.

Table 1. Experimental values used as reference and resulting parameters of equilibrated packing models.

experimental reference					modeling data			
polymer/gas	density polymer ^a / g cm ⁻³	p _{ref} / bar	C _{ref} /cm ³ (STP)/cm ³	$\Delta V/V_0$ / %	polymer/ name of state	# of atoms ^d	edge length of simulation cell / Å	density packing ^b / g cm ⁻³
PSU	1.240	0 ^c	0.0	0.0	<i>PSU</i>	5078 ^c	38.6	1.200
PSU/CH ₄	1.242	50	22.4	0.35	<i>PSU35</i>	+175 ^e	38.9	1.189
PSU/CO ₂	1.262	50	52.6	1.62	<i>PSU80</i>	+240 ^e	39.3	1.233
PI4	1.352	0 ^c	0.0	0.0	<i>PI4</i>	4482 ^c	38.6	1.273
PI4/CH ₄	1.342	50	69.4	0.89	<i>PI76</i>	+380 ^e	39.1	1.276
PI4/CO ₂	1.284	35	105.6	6.13	<i>PI156</i>	+468 ^e	39.8	1.359
PIM-1	1.124	0 ^c	0.0	0.0	<i>PIM</i>	4145 ^c	37.7	1.073
PIM-1/CH ₄	1.091	45	69.4	1.94	<i>PIM95</i>	+475 ^e	38.5	1.047
PIM-1/CO ₂	1.229	45	150.1	7.75	<i>PIM206</i>	+618 ^e	39.3	1.194

^a Density of the polymer/gas-system (target density for the packing models).

^b Obtained density of the packing model including the penetrant-molecules.

^c Bulk pressure of 1 bar for packing models.

^d Atoms per repeat unit: PSU: 54; PI4: 56; PIM-1: 55

^e Atom number of penetrants corresponding to the concentration in terms of penetrants per simulation cell.

Three models of each reference state (nonswollen, CH₄- and CO₂-swollen) were constructed to achieve reasonable statistics, and all results are presented as their arithmetic mean.

Table 1 summarizes the necessary data derived from combined sorption and dilation experiments which specify the two “states” observed in the experiment for every polymer/gas system, that represent the basis for the packing models, along with the data used for construction and resulting properties of the equilibrated packing models. The density value of every polymer/gas system, representing the “target” density for the attainable packing models, was calculated from the experimental sorption value C_{ref} and the experimental observed volume dilation $\Delta V/V_0$. Planning to construct atomistic models with about 5000 atoms, the experimental values were converted respectively into the presented numbers of polymer repeat units, and sorbed gas atoms. Table 1 contains also in the last two columns, the primary simulation result for the packing models, i.e. the mean edge length of the boxes and the obtained densities of the polymer/gas systems.

The experimental polymer matrix densities and those of the obtained packing models are presented in Table 2. For all three polymers, the simulated density values decrease (in agreement with the experimental values) from the “unswollen” pure system via the “swollen” polymer/gas systems with CH₄ to the lowest value for the polymer/CO₂ system. The deviation from the experimental value is in general below 5 %. This is an acceptable value for these very rigid glassy polymers. For the sorption properties of the polymer matrices, the *free volume* is a significant parameter. Table 2 contains fractional free volume (FFV) values in %, derived from the experimental densities. These values $FFV=V_f/V_{sp}$ were estimated using experimental density ρ and van der Waals volumes V_w of the atoms forming the repeat units. According to the Bondi method⁴⁷, the free volume of a polymer V_f (cm³/g) can be estimated as $V_f = V_{sp} - 1.3V_w$ where the specific volume V_{sp} is defined as reciprocal density ($1/\rho$), the

van der Waals volume is calculated using a group contribution method, and a universal “packing coefficient” equal to 1.3 is used to convert the van der Waals volume of the repeat unit in the occupied volume. Correlations of gas transport data in many polymers have been discussed and confirm the general usefulness of Bondi’s approach⁴⁸. It can be assumed that a large scatter of the empirical correlations of diffusion and permeability coefficients with V_f and FFV, which is often observed for various polymers, may be induced by the merely approximate nature of this equation.

Based on Bondi’s concept and our experimental data, the free volume of the three polymers increase in the order PSU<PI4<PIM in a ratio of 1.00:1.38:1.42. This ranking is also confirmed by the respective packing models. In⁴⁹ a method was proposed to estimate FFV values equivalently to Bondi’s from a simple geometrical analysis of packing models.⁴¹ The atoms of the polymer chain had been assumed to be represented by hard spheres with a radius derived from the van der Waals radius of the respective atoms (C: 1.55 Å; H: 1.10 Å; N: 1.40 Å; O: 1.35 Å; F: 1.30 Å; S: 1.81 Å). To determine the FFV, the cubic simulation cells were overlaid with a three-dimensional grid with a grid size of about 0.5 Å. At every grid point it was then tested if a hard sphere with radius r_{test} , would overlap with the hard spheres (HS) at the atom positions of the polymer. The FFV accessible for these probe molecules was then estimated by the ratio of grid points without overlap to the total number of grid points. In the above mentioned study⁴⁹, a test particle with a radius of $r_{\text{test}}=0.43$ Å yielded an acceptable agreement to values found by the Bondi method. This method was applied for all packing models with the result, that these FFV values confirm the increase in free volume during swelling for each investigated polymer, while maintaining the FFV ranking between the three polymers. As can be seen from the data in Table 2, the FFV values for PSU, PI4 and PIM increase according to this calculation method in a ratio of 1:1.42:1.55, which is in good qualitative agreement to the method of Bondi applied on the experimental density data. To

show the empirical character of the test particle-insertion method and at the same time emphasize its usefulness, the radius of the test particle was varied until a better quantitative agreement to the Bondi value of the pure PSU matrix was achieved. As can be seen in the rightmost column of Table 2 for a test particle with radius $r_{\text{test}}=0.473 \text{ \AA}$, the quality of the agreement to Bondi values of the swollen matrices increases. This indicates that by choosing a standard to calibrate the method, the free volume of polymer matrices under similar conditions may be characterized in a relative way. For comparison table 2 also includes FFV data obtained from the Synthia software of Accelrys which predicts polymer properties based on structure and topology of the repeat unit using group contribution and QSPR (quantitative structure property relationships) techniques, i.e. without explicit information on the solid density of the polymer.

3.3 Calculation of sorption isotherms

The (empty) atomistic packing models of the “swollen” and “nonswollen” state of the polymers (e.g. PSU for both gases, PSU35 for CH₄ and PSU80 for CO₂) were used to calculate CO₂- and CH₄-sorption isotherms, assuming a static polymer matrix and therefore exclusively using the free volume elements of the matrix as “sorption sites”. This was carried out by Monte Carlo simulations of a Grand Canonical ensemble (GCMC). This technique allows the calculation of the sorbed amount of gas in the free volume regions (sorbed phase s) at assumed phase equilibrium, $\mu^s(T,p) = \mu^g(T,p)$, with an ambient gas phase (superscript g) at a given temperature T and pressure p. The chemical potential (fugacity coefficient) in the gas phase for CO₂ and CH₄ at the specified T and p values were calculated with the help of the Peng-Robinson⁵⁰ equation of state. The amount and properties of the sorbed CO₂ (CH₄) molecules in free volume elements were calculated by statistic sampling of molecular configurations at constant μ , V, and T. Isotherm values have been calculated for pressures up to 50 bar gas pressure.

Table 2. Densities and fractional free volumes of experimental and simulated polymer/gas systems

polymer/gas	packing model	matrix densities ^a / g/cm ³		$\frac{\Delta\rho}{\rho_{\text{exp}}}$ / %	Fractional Free Volume (FFV) / %			
		experiment	<i>simulation</i>		experiment	<i>simulation</i>	<i>simulation (particle insertion)^c</i>	
					(Bondi) ^b	(Bondi) ^b	$r = 0.43\text{\AA}$	$r = 0.473\text{\AA}$
PSU	PSU	1.240	<i>1.200</i>	-3.2	13.5	<i>16.3</i>	<i>18.4</i>	<i>16.3</i>
PSU/CH ₄	PSU35	1.226	<i>1.173</i>	-4.3	14.5	<i>18.1</i>	<i>20.0</i>	<i>17.9</i>
PSU/CO ₂	PSU80	1.164	<i>1.136</i>	-2.4	18.8	<i>20.7</i>	<i>22.2</i>	<i>20.1</i>
PI4	PI4	1.352	<i>1.273</i>	-5.8	18.7	<i>23.4</i>	<i>26.1</i>	<i>24.0</i>
PI4/CH ₄	PI76	1.306	<i>1.242</i>	-4.9	21.5	<i>25.3</i>	<i>28.0</i>	<i>25.9</i>
PI4/CO ₂	PI156	1.113	<i>1.178</i>	+5.8	33.1	<i>29.2</i>	<i>31.3</i>	<i>29.4</i>
PIM-1	PIM	1.124	<i>1.073</i>	-4.5	19.2	<i>22.8</i>	<i>28.5</i>	<i>26.4</i>
PIM-1/CH ₄	PIM95	1.044	<i>1.003</i>	-3.9	24.9	<i>27.8</i>	<i>32.5</i>	<i>30.5</i>
PIM-1/CO ₂	PIM206	0.973	<i>0.946</i>	-2.8	30.0	<i>32.0</i>	<i>35.7</i>	<i>33.8</i>

^a Densities of the polymer excluding the penetrants.

^b Calculated by the *Synthia* software of Accelrys using the Bondi method using experimental density and mean density of the packing models, respectively.

^c Calculated from empty packing models assuming hard sphere radii for all atoms and using a test particle of radius r .

4 Results

In the following, we present the results of the sorption experiments and the corresponding GCMC simulations of the six polymer/gas systems, i.e., PSU/CO₂ and PSU/CH₄, PI4/CO₂ and PI4/CH₄ as well as PIM/CO₂ and PIM/CH₄. In the Figures shown below, open squares correspond to the experimental data, with a circle to indicate the high-pressure reference state. All (experimental and GCMC) sorption isotherms are fitted by an analytical equation, based on a simple sorption model. Here the Dual Mode Sorption Model (DM) is used as sorption data of small molecules in glassy polymeric materials are often discussed in terms of this model:

$$C(p) = k_D p + \frac{C'_H b p}{1 + b p} \quad (3)$$

Here, the pressure-dependent concentration of the penetrant molecule $C(p)$ is described by the Henry parameter k_D , representing sorption in interstitial free volume, whereas the Langmuir capacity C'_H and the affinity parameter b reflect sorption in “frozen-in” microcavities of the polymer. However, this debatable model will not be further discussed in this work, but since it is universally applied for data representation⁵¹ it will be used here to process and report the gathered data. The obtained DM parameters for the isotherms are summarized in Table 3.

The triangles pointing down represent the GCMC-sorption isotherm of the unswollen models, with an error-bar indicating the standard deviation due to the averaging procedure over three packing models, and a broken line representing the best fit of the Dual Mode model (parameters given in Table 3). Correspondingly, the upward pointing triangles (and associated error bars and broken line) represent the simulated sorption data of the swollen models.

a)

b)

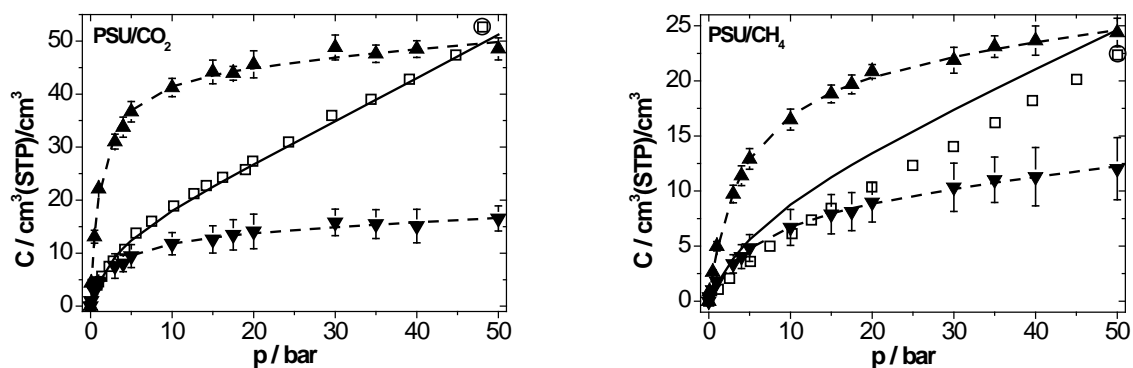


Figure 3. Sorption isotherms (308 K, 35 °C) for (a) PSU/CO₂, and (b) PSU/CH₄: calculated for the nonswollen (PSU; ▼) and swollen (a: PSU80m, b: PSU35m; ▲) packing models of PSU; experimental data (□); dual mode sorption fits (---) and linearly weighted average of the latter (—). The experimental reference for the swollen state is marked by a circle.

Figure 3a shows the experimental results of CO₂ sorption in polysulfone (open squares), along with the results of the corresponding GCMC simulation on the packing models of the unswollen and swollen reference states (up- and downward triangles, respectively).

As described above the broken lines ($C_{un}(p)$ and $C_{sw}(p)$ for the unswollen and swollen GCMC-isotherm data, respectively) stand for a best fit of equation 3 to represent each set of simulated data to be combined to a single curve $C_{sim}(p)$ as will be explicated in the following. As the data for PSU were already discussed in ref. ⁴, only the main aspects will be repeated at this point: The individual data of each reference state (i.e. packing model) only agree with the experimental data in the immediate pressure range and hence density state of the dilating polymer at the specified pressure. This is an expected result, since the GCMC calculations are performed on a static packing model, i.e. CO₂ penetrants are positioned in possible sorption sites and no changes of the polymer matrix due to sorption are taken into account. For the unswollen packing model this entails a "filling up" of only few sorption sites, agreeing with the experimental data only within the pressure range up to about 5 bar. At larger pressures the Gibbs free energy of the system cannot be reduced by the insertion of more penetrant

molecules and the capability of the matrix to accept further penetrants is rapidly reduced. Conversely, the swollen model provides an unrealistic amount of free volume at small pressures, which is equally "filled up" at the first pressure steps meeting the experimental data not before the chosen reference state in the high pressure range. But, these two sorption isotherms, resulting from GCMC simulation may be combined using a linearly weighted average as expressed by the following equation:

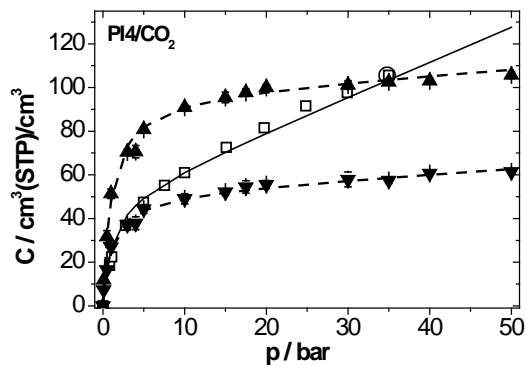
$$C_{sim}(p) = \left(1 - \frac{p}{p_{sw}}\right)C_{un}(p) + \frac{p}{p_{sw}}C_{sw}(p) \quad (4)$$

Here, p_{sw} denotes the pressure of the swollen reference state and $C_{un}(p)$ and $C_{sw}(p)$ are the dual mode representations of the unswollen and swollen data sets which are to be combined to the single curve $C_{sim}(p)$. Under the assumption of a linear change in density with pressure, as adopted by Doghieri and Sarti in their NET-GP-model^{52, 53, 54, 55} and further assuming the relationship between density and concentration to be linear as well, equation (4) mathematically achieves a transition between the GCMC sorption isotherms of the unswollen and swollen models, respectively. As a result the simulated curve excellently agrees with the experimental data (solid line in Figure3a). Similar results could be achieved for the other investigated polymer gas systems. Figure3b shows the results for the PSU/CH₄-system. Again, the GCMC sorption isotherms of a single reference state do not agree with the experimental data over the whole investigated pressure range. However, constructing the combined curve by linear transition, results in reasonably well agreement of simulated and experimental data.

Figures 4a and b show the simulated and experimental sorption isotherms of CO₂ and CH₄ in PI4, respectively. It should be noted that the reference pressure p_{sw} for the PI4/CO₂-system has been chosen at 35 bar for technical reasons but the GCMC calculations were performed up to 50 bar, hence the deviation at large pressures. Again the simulated combined curve

agrees quite well with experimental data, showing a slight deviation for methane sorption similarly to the polysulfone/CH₄ result (Figure 3b).

a)



b)

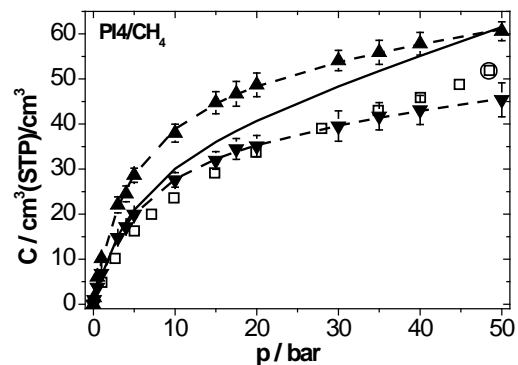
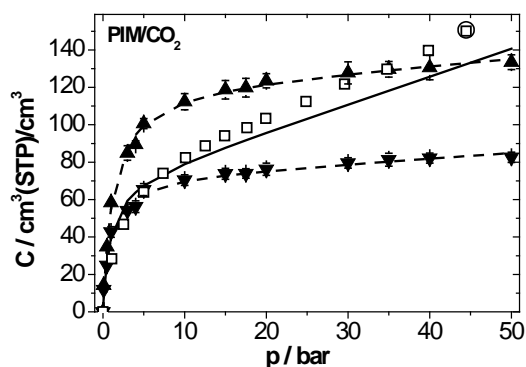


Figure 4. Sorption isotherms (308 K, 35 °C) for (a) PI4/CO₂, and (b) PI4/CH₄: symbols and linestyles for the experimental and simulated data (*PI76m* and *PI156m*) are chosen in accordance to Figure 3.

a)



b)

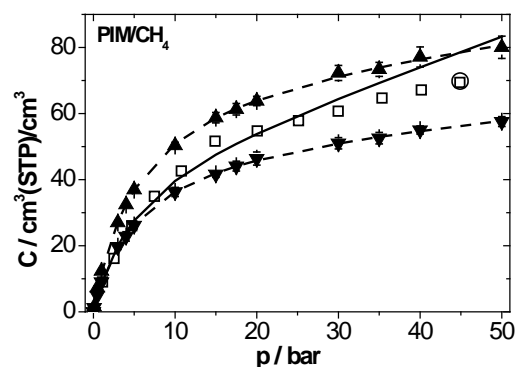


Figure 5. Sorption isotherms (308 K, 35 °C) for (a) PIM-1/CO₂, and (b) PIM-1/CH₄: symbols and linestyles for the experimental and simulated data (*PIM95m* and *PIM206m*) are chosen in accordance to Figure 3

Results for the CO₂ and CH₄ sorption in the polymer of intrinsic microporosity PIM-1 are depicted in Figure 5. Here, the massive sorption capacity for CO₂ as determined

experimentally is slightly underestimated by the simulated combined curve, but the agreement is still acceptable.

In order to compare our experimental data on PIM-1 with results from Fang et al.³⁶ and Budd et al.³⁴ solubility coefficients S at low pressures may be calculated using the Dual Mode representation given in table 3. For PIM-1 we obtain experimental solubility coefficients of 36 and $8.3 \text{ cm}^3(\text{STP})/\text{cm}^3(\text{polymer}) \text{ bar}$ for CO_2 and CH_4 at 308 K (35 °C) and 200 mbar, respectively. Fang et al. report for CO_2 66.9 (experimental) and $50.7 \text{ cm}^3(\text{STP})/\text{cm}^3(\text{polymer}) \text{ bar}$ (simulated), for CH_4 13.7 (experimental) and $14.2 \text{ cm}^3(\text{STP})/\text{cm}^3(\text{polymer}) \text{ bar}$ (simulated), both at 303 K (30 °C) and 200 mbar. Note that the data refer to different temperatures and were obtained by different methods. Our data were obtained from gravimetric sorption measurements while data of Budd et al. were calculated from time-lag experiments. In this context also the strong dependence on film formation and history, as reported in³⁵ have to be taken into account.

Table 3. Dual Mode sorption data of experimental CO₂ and CH₄ sorption and corresponding GCMC-Simulations.

polymer/gas	experimental data			modelling data					
				unswollen model (C _{un} (p))			swollen model (C _{sw} (p))		
	k _D ^a	C' _H ^b	b ^c	k _D ^a	C' _H ^b	b ^c	k _D ^a	C' _H ^b	b ^c
PSU/CH ₄	0.381	3.35	0.206	0.076	9.4	0.176	0.073	22.7	0.247
PSU/CO ₂	0.805	12.8	0.384	0.066	14.0	0.384	0.113	45.2	0.815
PI4/CH ₄	0.482	31.5	0.153	0.187	40.4	0.179	0.229	54.4	0.205
PI4/CO ₂	1.56	54.6	0.544	0.243	51.6	0.931	0.254	96.4	0.980
PIM-1/CH ₄	0.116	76.4	0.109	0.195	53.3	0.183	0.270	74.5	0.183
PIM-1/CO ₂	1.64	78.6	0.480	0.269	72.6	1.165	0.321	121.9	0.815

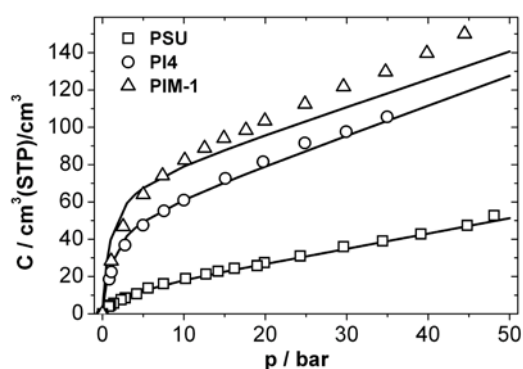
^a cm³(STP)/cm³bar⁻¹ ^b cm³(STP)/cm³ ^c bar⁻¹

5 Conclusions

Sorption and dilation characteristics of three polymers (PSU, PI4 and PIM-1) in contact with two gases (CO_2 and CH_4) have been investigated utilizing experimental characterization methods and techniques of detailed atomistic molecular modeling. The density and concentration data at the minimum and maximum pressure of each experimental sorption and dilation isotherm were chosen as reference states to construct detailed molecular packing models of the nonswollen and swollen state of each polymer/gas system. Free Volume analyses have been performed by test particle insertion and it was shown, that by calibrating the test particle radius to a standard, good qualitative agreement to an estimation of the free volume using the Bondi method can be obtained.

Grand Canonical Monte Carlo (GCMC) simulations were performed to obtain simulated sorption isotherms for the nonswollen and swollen state, respectively, and a linear transition with pressure was proposed that achieves mostly excellent agreement to the experimental data.

a)



b)

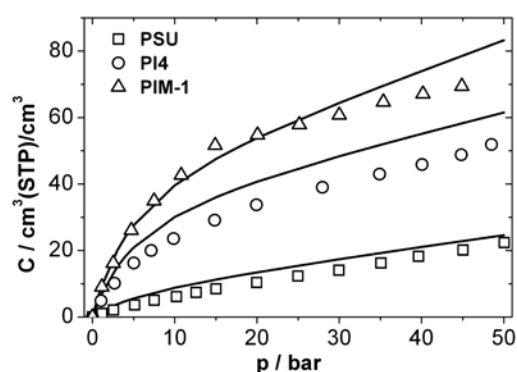


Figure 6. Sorption data (308 K, 35°C) of CO_2 (a) and CH_4 (b) in the polymers PSU (\square), PI4 (\circ), and PIM-1 (\triangle), along with the corresponding linearly weighted average of GCMC simulation results \longrightarrow .

The experimental sorption data of CO₂ for all three polymers along with the results of the GCMC simulation are summarized in figure 6a. To retain lucidity, the simulation results are represented by single curves superimposing unswollen and swollen state data using equation (4) as described above. Besides the good agreement between experimental and simulated results, it can be concluded that sorption capacity highly depends on the amount of accessible free volume. The calculation of the Free Volume by way of the Bondi-method shows (see Table 2) that the polymers, according to the amount of their FFV, are ordered as PSU << PI4 < PIM-1. Qualitatively, the same order is found for the sorption capacity C'_H of the dual-mode fit of the experimental data and of the swollen reference state $C_{sw}(p)$, which – despite the limits of the model - can be taken as a measure for the overall sorption capacity (cf. Table 3).

The same qualitative agreement can be observed from the CH₄ sorption results of both, experiment and simulation.

The method to simulate sorption isotherms, as proposed in this work, using experimental input of two reference states and combining the GCMC simulations on both states, has in effect no predictive character. However, the fact that the interpolation over a wide pressure range shows well agreement to experimental data validates the packing models as well as the general approach for three different classes of membrane polymers. Furthermore, if reasonable assumptions are made regarding the dependency of the density change on pressure, the presented method is capable to afford reasonable first approximation predictions in a moderate pressure range.

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