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Calculation of the Free Energy for Gas Absorption in Amorphous Polypropylene

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ABSTRACT: A computational strategy for the prediction of the excess free energy of gases (helium, hydrogen, nitrogen, oxygen, and methane) in amorphous polymers is presented. It involves a detailed atomistic description of the polymer–gas system. From the free energy Henry's law constants and solubility coefficients can be calculated. Samples of amorphous atactic polypropylene are generated by the technique of Theodorou and Suter. The excess free energy for the absorption of various species of gas molecules is calculated via a test-particle-insertion method and classical molecular dynamics. The results are compared to experimental data where available.

1. Introduction

The thermodynamics of the solvation of penetrant gas molecules in polymers can be described by the dual-mode sorption equation[1,2]

$$c_p = Sp + C\frac{bp}{1 + bp} \qquad (1.1)$$

where c_p is the molarity of the penetrant molecules dissolved in the polymer (in mol/m^3) being in equilibrium with the vapor of pressure p (in Pa). The first term corresponds to a genuine solvation process, and S is the solubility constant which is proportional to Henry's law constant $K_H = c_p/c_g$. (In this article we define Henry's law in terms of the molarities of the penetrant in the gas phase and in the polymer, respectively, rather than in terms of pressure and mole fraction.) The second term is a Langmuir-type isotherm corresponding to sorption of gas into specific sorption sites in the polymer, and C and b are the Langmuir capacity and affinity constants, respectively. The relative importance of the two terms in eq 1.1 can vary considerably from one polymer to another. In the case of rubbers, for example, the second term can safety be neglected.[1] We confine the present development to the linear regime of eq 1.1.

Experimental solubility coefficients are customarily expressed as[3]

$$S = \frac{V_g(\mathrm{STP})}{V_p p} \qquad (1.2)$$

denoting the volume of gas V_g(STP) at standard temperature and pressure (STP: $T_0 = 273.15$ K, $p_0 = 101\,300$ Pa) absorbed in a volume V_p of polymeric material given an actual gas pressure p. This gives rise to a unit for S of cm^3(STP)/(cm^3 Pa). Assuming ideal gas behavior for the penetrant gas both at the actual temperature and pressure and at the standard temperature and pressure, the pressure and the absorbed volume of gas can be expressed in terms of the molarities of the penetrant in the gas phase and in the polymer

$$p = \frac{nRT}{V} = c_g RT$$

$$\frac{V_g(\mathrm{STP})}{V_p} = \frac{nRT_0}{V_p p_0} = c_p\frac{RT_0}{p_0} \qquad (1.3)$$

Here, V is the volume, T is the actual absolute temperature, and R is the gas constant ($R = 8.314\,41$ J K^{-1} mol^{-1}). Inserting eq 1.3 into eq 1.2 yields the relation between the solubility coefficient and Henry's law constant

$$K_H = \frac{Tp_0}{T_0}S \qquad (1.4)$$

The Henry's law constant is related to the excess (nonideal-gas) part of the free energy ΔA_{ex} of the polymer–penetrant system in the limit of zero penetrant concentration[4]

$$\Delta A_{ex} = -kT \ln K_H \qquad (1.5)$$

Free-energy-related quantities can be calculated by a variety of molecular simulation methods.[5,6] We choose a test-particle-insertion method similar to Widom's method[7] which has been successfully applied to one-component and binary liquids but, as far as we know, not to polymeric systems. For detailed descriptions of the method, see, e.g., refs 8–10. Equilibrated starting configurations of the pure host polymer are generated using the Monte Carlo procedure of Theodorou and Suter.[11] Thermal motion of the polymer chain is accounted for by subjecting these configurations to molecular dynamics (MD) calculations.

2. Theoretical and Computational Methods

In the canonical ensemble the equilibrium constant K_H for the reaction

$$\mathrm{A(gas\ phase)} \leftrightarrow \mathrm{A(polymer)} \qquad (2.1)$$

at constant volume V and temperature T is given as

$$K_H = \frac{Q_p(N,V,T)}{Q_{id}(N,V,T)} \qquad (2.2)$$

The canonical partition function for the gas dissolved in the polymer is denoted as $Q_p(N,V,T)$ and the one for the gas phase as $Q_{id}(N,V,T)$, with the subscript indicating that

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ideal gas behavior is assumed. The partition function for the penetrant in the polymer can be separated into an ideal gas part and an "excess" part $Q_{ex}(N,V,T)$

$$Q_p(N,V,T) = Q_{id}(N,V,T)\,Q_{ex}(N,V,T) = \frac{V^N}{N!\Lambda^{3N}}Q_{ex}(N,V,T) \quad (2.3)$$

($\Lambda = (h^2/2\pi mkT)^{1/2}$) so that eq 2.2 becomes

$$K_H = Q_{ex}(N,V,T) \quad (2.4)$$

It is further assumed that gas molecules sorbed in the polymer only interact with the polymer matrix and not with one another. This constitutes the ideal dilute solution limit for which Henry's law is applicable. Under these circumstances $Q_{ex}(N,V,T)$ can be approximated by the product of one-particle partition functions

$$Q_{ex}(N,V,T) \approx [Q_{ex}(1,V,T)]^N \quad (2.5)$$

The one-particle excess partition function is given by

$$Q_{ex}(1,V,T) = \frac{Z(1,V,T)}{V} = \frac{\int_V \exp(-\Delta E/kT)\,\mathrm{d}\mathbf{r}}{\int_V \mathrm{d}\mathbf{r}} = \langle\exp(-\Delta E/kT)\rangle \quad (2.6)$$

Here, ΔE is the potential energy change upon insertion of a single penetrant molecule into the host polymer.

Inserting eq 2.6 into eq 2.4 yields for the equilibrium constant

$$K_H = \langle\exp(-\Delta E/kT)\rangle^N \quad (2.7)$$

and the free-energy change for reaction (2.1) is given by

$$\Delta A = -kT\ln K_H = -RT\ln\langle\exp(-\Delta E/kT)\rangle \quad (2.8)$$

(N is taken to be Avogadro's number.) Note that the free energy for the reaction is equal to the excess free energy ΔA_{ex} of the penetrant in the polymer. Because of the approximation introduced in eq 2.5, eq 2.8 holds only in the vicinity of the ideal dilute solution of the penetrant in the polymer, i.e., in the limit of zero penetrant concentration or zero pressure in the gas phase. It is worth noting that Gusev and Suter[12] have recently developed a method which allows the calculation of solubilities at finite penetrant concentrations but which disregards the thermal motion of the host polymer and treats it as a static background.

It should be noted that the above derivations are based on the canonical ensemble, i.e., conditions of constant temperature and volume. The experimental measurements are usually carried out at constant temperature and pressure, i.e., in the isothermal–isobaric ensemble, and the appropriate free energy is the Gibbs free energy G rather than the Helmholtz free energy A. However, in the absence of specific favorable interactions the solubility of permanent gases in polymers is very low and they do not induce any structural changes in the polymer such as swelling.[13] This is explained by the notion that sorbed gas molecules tend to occupy preexisting voids in the polymer. Therefore, in the particular cases studied here, the canonical ensemble should be a reasonable approximation.

Equation 2.8 provides the recipe for the test-particle-insertion method for the calculation of the excess free energy. A test molecule, which models the gas molecule under study, is repeatedly inserted into the polymer system, and the would-be changes in the total energy ΔE caused by these insertions are calculated. The test molecule is never actually left in the system. The free energy is expressed as the average of the Boltzmann factor of the test-particle insertions according to eq 2.8. The Boltzmann factor may be interpreted as the acceptance probability for a hypothetical Monte Carlo (MC) move which inserts a molecule into the system. The configurations of the polymer into which the test particle is inserted have to sample adequately the microstates corresponding to the state point of the system. They may therefore be generated by either MD or MC simulations of the pure polymer.

One advantage of the test-particle-insertion method is that the excess free energy for several gas species may be calculated from a single set of polymer configurations. Because of the computational cost of calculating a trajectory of adequate length (on the order of nanoseconds), this method is more economical than other popular methods for the calculation of free energies, such as thermodynamic integration and perturbation methods,[5,6] which require separate MD or MC calculations for every penetrant species. On the other hand, in practice the method is limited to small penetrant molecules, since it is very likely that a randomly inserted large molecule will have a strong overlap with one of the polymer's atoms. This leads to a large positive ΔE and an extremely low "acceptance probability" so that the statistics of the test-particle's Boltzmann factor will be poor and very long simulations will be required. However, in the case of liquids of small molecules the method has been shown to be reliable at reasonable liquid densities, both for one-component liquids[9] and binary mixtures.[10]

The energy change upon insertion of a gas molecule into the polymer matrix is given as

$$\Delta E = \sum_{i=1}^{n} E_i + E_{lrc} \quad (2.9)$$

where the E_i are the interactions of the gas molecule with the n atoms of the polymer (a monatomic gas molecule is assumed in this development, the generalization to rigid polyatomics being straightforward).

$$E_i = \begin{cases} C_{12,i}/R_i^{12} - C_{6,i}/R_i^{6}, & R_i \le R_{cut} \\ 0, & R_i > R_{cut} \end{cases} \quad (2.10)$$

Here, the distance between the inserted gas molecule and the polymer atom i is denoted as R_i, $C_{12,i}$ and $C_{6,i}$ are the Lennard-Jones coefficients for this interaction, and R_{cut} is a cutoff distance. The long-range correction term E_{lrc} in eq 2.9 is given as

$$E_{lrc} = \frac{4\pi}{9V}\sum_{i=1}^{n}\left[\frac{C_{12,i}}{R_{cut}^{\;9}} - 3\frac{C_{6,i}}{R_{cut}^{\;3}}\right] \quad (2.11)$$

Many trial insertions of the test molecule are done into each configuration of the polymer, the energy changes are calculated, and the Boltzmann factors of eq 2.8 are evaluated and averaged. Since a finite number of trial insertions only samples part of the available conformation space of the test particle, there is the possible danger that important contributions to the free energy are missed by the method. We find that a number of insertions per polymer configuration of 10 000 is sufficient to stabilize the computed free energy, even in the case of the largest penetrant molecule of this study, methane. The insertion positions (and in the case of the diatomics also the orientations) are chosen at random. In many of the previous applications of the Widom method, insertions of

Table I
Lennard-Jones Site–Site Interaction Parameters and Bond Lengths *l* (Diatomics Only) of Penetrant Molecules

molecule	l/nm	C_6/(kJ mol^{-1} nm^6)	C_{12}/(kJ mol^{-1} nm^{12})	ref
He		9.4593×10^{-5}	2.6377×10^{-8}	*a*
H_2	0.074116	1.9439×10^{-4}	2.9998×10^{-8}	*b*
N_2	0.1090	1.6315×10^{-3}	2.1456×10^{-6}	*c*
O_2	0.121	1.3498×10^{-3}	8.8960×10^{-7}	*d*
CH_4		1.5241×10^{-2}	4.7134×10^{-5}	*a*

[a] Hansen and McDonald.[8] [b] Suter and Flory.[18] [c] Cheung and Powles.[22] [d] English and Venables.[23]

a fixed lattice of test particles have been used.[9] This is well justified for liquids where the motion of the host molecules provides for sufficient randomness of the local environment at the insertion points. In polymers with their relaxation times much longer than in liquids we believe it is safer to perform random insertions, although we have not put this hypothesis to the test. A well-tested random number generator is used for this purpose.[14]

The generation of amorphous polypropylene starting structures follows closely the procedure of Theodorou and Suter.[11] The polypropylene chain of appropriate tacticity is grown in the presence of cubic periodic boundary conditions. The conformational statistics of the backbone dihedral angles are given by the rotational isomeric state theory.[15] However, the probability distribution is modified to include the effects of nonbonded interactions and periodic boundary conditions. The length of the simulation cube is 1.8154 nm, which is kept throughout all simulations. The chain contains 76 monomer units plus end groups. The macroscopic density of the system is thus 891.4 kg m^{-3}. In order to eliminate local strain, the structure is energy minimized using the Shanno variant of the conjugate-gradient method.[16] The polypropylene sample is further relaxed by 200 ps of MD before sampling commences.

A molecular dynamics simulation of the pure polypropylene of 2-ns duration is performed, during which configurations are written every 1 ps. The leap-frog algorithm with a time step of 2 fs is used. The temperature is maintained constant at 300 K by means of the loose-coupling algorithm of Berendsen et al.[17] using a coupling time of 1 ps. For polypropylene the force field of Suter and Flory[18] is used, augmented by bond-angle and improper dihedral terms. Details are given elsewhere.[19] The bond distances are constrained by the SHAKE method.[20] All energy minimizations and MD simulations are performed using the YASP package.[21]

The test particles interact with the polypropylene host through a Lennard-Jones site–site potential (cutoff distance, 0.9 nm). The atomic interaction parameters are listed in Table I. For mixed interactions the Lorentz–Berthelot mixing rules[5] are used. Table I also lists the bond lengths for the diatomic penetrant species used in the calculation. Note that methane is modeled as a single interaction site.

3. Results and Discussion

The calculated excess free energies for He, H_2, N_2, O_2, and CH_4 in amorphous polypropylene are given in Table II. These are calculated from the whole 2-ns simulation. The free energies have also been calculated for separate 100-ps pieces of the MD trajectory. These are displayed in Figure 1. Two main features can be seen on this figure: (1) In the sequence He–H_2–N_2–O_2–CH_4 the free energy decreases; i.e., the latter species dissolve more easily than the former. (2) The fluctuation between different subaverages increases in the order He–H_2–O_2–N_2–CH_4.

Table II
Excess Free Energies (kJ mol^{-1}) for Penetrant Molecules in Amorphous Atactic Polypropylene

molecule	ΔA_{ex}(calc), this work	ΔA_{ex}(exptl)	ref
He	5.12	10.32	*a*
		21.91	*b*
H_2	0.400	4.75	*b*
Ne		9.53	*a*
N_2	−1.20	7.02	*a*
O_2	−3.72		
Ar		5.69	*a*
CH_4	−6.09		

[a] Polyethylene–polypropylene copolymer containing 31 methyl groups per 100 carbon atoms.[27] [b] Polypropylene (crystallinity, 50%; density, 907 kg m^{-3}), derived from permeability and diffusion coefficient.[3]

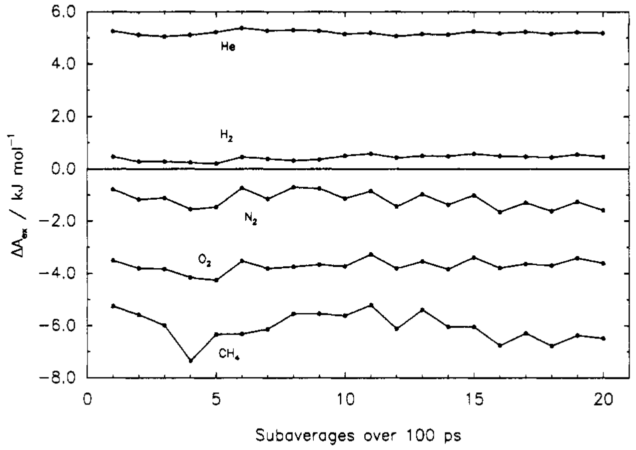

Figure 1. Excess free energies calculated by test-particle insertion for separate 100-ps pieces of the polypropylene MD trajectory.

Both observations can be understood in the framework of the size of the penetrants and the strength of their interaction with the polymer matrix. For a Lennard-Jones potential these are conveniently represented by the effective radius σ of the penetrant and the strength of its interaction ϵ

$$\sigma = \left(\frac{C_{12}}{C_6}\right)^{1/6}, \quad \epsilon = \frac{C_6^{\,2}}{4C_{12}} \tag{3.1}$$

A trial insertion will be "successful", i.e., contribute appreciably to the free energy, if it hits an empty space in the host polymer. The free volume in an amorphous polymer is unevenly distributed: there are many more small than large cavities, which has been shown for amorphous polypropylene.[24] This means that the number of small cavities is more likely to remain essentially unchanged between two polymer configurations than the number of big cavities. If the size is big enough, such cavities may altogether disappear and reappear between two configurations, in which case the calculated free energy for a large molecule will be very different.

This finding is of technical importance. The fact that the He and H_2 subaverages in Figure 1 show hardly any scatter means that for these molecules reliable free energies can be obtained from much shorter simulations (a few hundred picoseconds). The fluctuation of the methane subaverages, on the other hand, indicates that the 2-ns simulation is just about sufficient to provide a converged free energy for this molecule. Penetrants bigger than methane probably need much longer simulation times. Ideally, one should also use MD trajectories from many different starting configurations in order to improve the prediction. Unfortunately, this is at present impossible

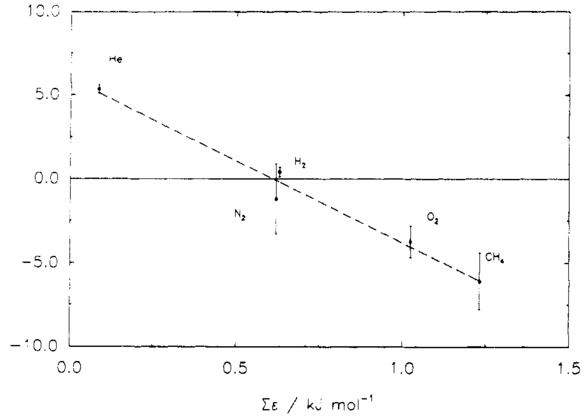

Figure 2. Excess free energies calculated from the entire 2-ns polypropylene MD trajectory related to the Lennard-Jones energy parameters ϵ of the penetrants used in the calculation. The error bars indicate the scatter between free energies calculated for the different polypropylene configurations. The dashed line represents a least-squares fit to the data (correlation coefficient, −0.989).

due to the prohibitive computational costs. Small cavities are also more easily sampled by the insertion method than large cavities since there are more of them. Therefore, for small molecules one can establish the free energy for a single polymer configuration by fewer trial insertions. In fact, subaverages for helium calculated with 5000 insertions/configuration cannot be distinguished from the ones with 10 000 insertions on the scale of Figure 1.

The absolute magnitude of the free energy depends on the strength of the interaction between the polymer and the penetrant. Provided the polymer configuration is exhaustively probed by the trial insertions, i.e., there are sufficient successful insertions, their energy contribution will be related to ϵ. This relation is made more explicit in Figure 2, which shows the free energy as a function of the sum of the site-site Lennard-Jones energies $\sum\epsilon$ of the penetrant. The error bars indicate the scatter between free energies calculated for the different polypropylene configurations. In spite of the crude reasoning, Figure 2 exhibits a linear relationship to a good approximation. At least-squares fit to the datapoints is indicated by the dashed line. Similar linear relationships between the logarithm of the solubility constant and quantities related to the interaction energy of the penetrant, for example, boiling temperature or critical temperature, are commonly reported in the literature.[13,25,26]

The direct comparison of the calculated excess free energies with experimental results is difficult since there seems to be no published data for amorphous atactic polypropylene. It is, however, useful to put the results of this work into perspective, without placing too much emphasis on the numerical values. Table II contains experimental data of related systems. One series of results is calculated from solubilities of penetrants in an amorphous polyethylene-polypropylene copolymer with a high proportion of propylene.[27] Of the penetrants studied here, He and N_2 are included in that study. The other study[3] only reports permeabilities P and diffusion coefficients D for He and H_2 in semicrystalline polypropylene of a higher density than studied here. From these data solubilities can, in principle, be derived as

$$S = P/D \tag{3.2}$$

The two He values differ substantially. It is therefore also difficult to say how much can be inferred from the H_2 result. Where both theoretical and experimental data are available, the theoretical free energies appear to be 4–8 kJ mol^{-1} lower than the experimental results. This comes close to the "magic kilocalorie" typical for predictions of free energy differences by molecular simulation which is encouraging given that the theoretical and the experimental polymer systems are related but not quite the same. The most likely source of discrepancy is the semicrystallinity (50%) of the polypropylene used in the experiment which should substantially lower the solubility compared to a completely amorphous system. Moreover, since atactic polypropylene does not form crystallites, there must be a large fraction of isotactic polypropylene in the experimental material. The difference between the free energies of He and N_2 is 3 kJ mol^{-1} experimentally and 6 kJ mol^{-1} theoretically, and between He and H_2 it is 6 kJ mol^{-1} experimentally and 5 kJ mol^{-1} theoretically. This indicates that free energy differences and relative solubility constants may be easier to predict than absolute solubility constants. This may be of importance for the prediction of the selectivity of polymers to different penetrant species.

In summary, it may be said that the computational approach to excess free energies, and hence solubilities, for penetrants in amorphous polymers outlined in this contribution provides results which are internally consistent and reasonably close to experimental values. This may pave the way for the prediction of permeabilities of polymers entirely by molecular simulation methods since diffusion coefficients for these systems, which form the other ingredient (eq 3.2), have recently been calculated by molecular dynamics[19,28-31] and Monte Carlo[32,33] methods.

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