Macromolecules **1993,** *26,* 6180–6183

Simulation of the Solubility of Alkanes in Polyethylene

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Received February 25, 1993; Revised Manuscript Received August 17, 1993[⊗]

ABSTRACT: Novel methods for simulation of the chemical potential and for simulation of phase equilibria in systems of chain molecules have been developed. These methods are applied here to simulate Henry's constants and solubility for linear alkanes in polyethylene. The results of our simulations are in good agreement with experiment. At moderate pressures, the solubility of an alkane in polyethylene exhibits strong deviations from ideal behavior, thereby rendering Henry's law of little use; our solubility simulations, however, are able to reproduce the experimentally observed saturation of the polymer by the alkane. For low concentrations of the solute in the polymer, simulations reveal the presence of "pockets" in the polymer in which solubility occurs preferentially. At higher concentrations, the distribution of the solute in the polymer becomes relatively uniform.

Introduction

Studies of solubility in polymers modeled in atomistic detail have been scarce. Further, these studies have been limited to small, spherical solutes at infinite dilution.[1,2] This scarcity has partly been due to shortcomings in available methods for simulation of chain molecules and, most notably, to limitations of existing techniques for simulation of the chemical potential of the solute in the polymer. In a recent publication we have presented a method for estimating the chemical potential of chain molecules by computer simulation.[3] That study, however, was devoted to testing and discussing the so-called continuum-configurational-bias (CCB) methodology for sampling the free energy of dense macromolecular systems.

At low to intermediate pressures, the solubility of a solute in a solvent can be estimated from Henry's law.[4] The chemical potential of a solute in a solvent at infinite dilution is of interest because it is directly proportional to Henry's constant for the solute in the solvent.[5] Here we present results of simulations of Henry's constants for alkanes dissolved in polyethylene melts.

At moderate to high pressures, deviations from ideal behavior become significant.[4,6] Gas sorption can no longer be described by Henry's law, and alternative means for estimating solubility are required. Further, these deviations increase as the solubility of the penetrant increases. We have therefore developed a second method for simulation of phase equilibria for systems of chain molecules.[7] We refer to such a method as the continuum configurational bias Gibbs-ensemble method (CCBG). In our original publication, only the simulation of phase equilibria for pure alkanes was discussed; here we use the CCBG method to simulate the solubility of intermediate-size solutes in polymers.

More specifically, the CCBG method is applied here to the simulation of the solubility of pentane in polyethylene. As expected, at low pressures both our Henry's constant calculations and our CCBG simulations yield equivalent results; at intermediate to high pressures, however, only the Gibbs-ensemble calculations provide satisfactory results.

Theoretical Aspects

Definition of Henry's Constant. The residual chemical potential for a solute in a solvent at infinite dilution is generally estimated by Widom's test-particle method according to

$$\mu^{\mathrm{r}} = -\frac{1}{\beta}\ln\langle\exp(-\beta U_{\mathrm{g}})\rangle_N \tag{1}$$

where $\beta = kT$ and U_{g} is the potential energy felt by a ghost solute particle in the host solvent.[8] The brackets with subscript N denote an average performed in an ensemble comprising N solvent particles. The ghost particle experiences an energy U_{g} from its interaction with the solvent, bot solvent particles do not feel the ghost.

The residual chemical potential of a solute is given by the difference between the chemical potential of the solute dissolved in the solvent and that of an ideal gas at the same temperature. For a fluid of simple spherical particles, the chemical potential of the ideal gas is given by

$$\beta\mu^{\mathrm{id}} = \ln\rho + h(\beta) \tag{2}$$

where ρ is the density of the ideal gas and $h(\beta)$ is a function only of β.

Henry's law states that the solubility of solute α (S_α) in solvent s is directly proportional to the pressure P

$$S_\alpha = P/H^{(\alpha)} \tag{3}$$

Henry's constant for a monatomic solute α is a solvent is therefore related to the infinite-dilution residual chemical potential $\mu^{\mathrm{r},\infty}$ through

$$H^{(\alpha)} = \frac{1}{\beta}\rho_{\mathrm{s}}\exp(\beta\mu^{\mathrm{r},\infty}) \tag{4}$$

where ρ_{s} is the molar density of the pure solvent. The chemical potential of solute α at infinite dilution is obtained by applying Widom's test-particle method (eq 1) for a test solute particle interacting with pure solvent.

If, however, solute α is a polyatomic molecule with additional internal degrees of freedom (e.g., torsions around carbon–carbon bonds in alkanes), eq 2 must be modified slightly. If the ideal gas is defined as a fluid in which different molecules do not interact with each other (intermolecular interactions are absent) but where different atoms of a molecule interact with each other (intramolecular interactions are considered), then the chemical potential of such a fluid is given by

$$\beta\mu^{\mathrm{r}} = \ln\rho + h'(\beta) - \ln\langle\exp(-\beta U_{\mathrm{intra}})\rangle_0 \tag{5}$$

where U_{intra} corresponds to the potential energy of an isolated chain molecule. The brackets in eq 5 indicate an average value, and subscript 0 denotes a property evaluated

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[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

0024-9297/93/2226-6180$04.00/0

for an isolated molecule. Here, U_{intra} includes only intramolecular contributions to the energy arising from pairwise interactions between atoms of the same molecule and from torsions around the internal configurational degrees of freedom. Other contributions to the intramolecular energy (e.g., from vibrational degrees of freedom) are grouped into the function $h'(\beta)$.

If contributions to the intramolecular energy of solute α other than those included in U_{intra} are assumed to be the same in the gas and in the solvent phases, then Henry's constant of the solute is given by

$$H^{(\alpha)} = \frac{1}{\beta}\rho_s \frac{\langle \exp(-\beta U_{\text{intra}})\rangle_0}{\langle \exp(-\beta[U_{\alpha,s} + U_{\text{intra}}])\rangle} \qquad (6)$$

where $U_{\alpha,s}$ is the energy arising from intermolecular interactions between the solute test particle and the solvent and the average in the denominator is performed in a canonical (NVT) ensemble.

For calculations of solubility in polymers, it is customary to express Henry's constants on a weight-fraction basis.[9] This practice stems from the fact that Henry's constants defined in this manner exhibit little or no dependence on the molecular weight of the polymer. Equation 6 is therefore rewritten as

$$H_w^{(\alpha)} = \frac{1}{\beta}\rho_s \frac{M_s}{M_\alpha} \frac{\langle \exp(-\beta U_{\text{intra}})\rangle}{\langle \exp(-\beta[U_{\alpha,s} + U_{\text{intra}}])\rangle} \qquad (7)$$

where M_α and M_s denote the molecular weights of the solute and the polymer, respectively. Weight fractions of the solute in the polymer are calculated according to

$$w_\alpha = P/H_w^{(\alpha)} \qquad (8)$$

Equation 7 constitutes the basis for our subsequent calculations of Henry's constants. Note, however, that it is only valid for a particular and arbitrary definition of the ideal gas state and it is subject to the validity of the assumptions mentioned above.

Simulation of Henry's Constants. In practice, a problem arises when eq 7 is applied to the calculation of Henry's constants for long, articulated molecules: since it relies on a random sampling of the potential-energy surface of the host system, most random insertions of the test molecule will give rise to steric overlaps and will be rejected; consequently, statistics will be poor. This problem can be overcome to some extent by employing a biased insertion scheme designed to avoid overlaps between test particle and the host system.[3] The so-called CCB test-particle method provides such a scheme.

In the CCB test-particle method, the first segment of an articulated test molecule is placed at a random point. Subsequent segments of the molecule are placed in a stepwise manner until a full test molecule is grown. The procedure by which test molecules are grown has been outlined in detail elsewhere and need not be given again.[10] Suffice it here to say that it involves the computation of a "Rosenbluth" weight, W (we follow here the notation of de Pablo et al.[10]), which is incorporated into the calculation of the chemical potential according to

$$H_w^{(\alpha)} = \frac{1}{\beta}\rho_s \frac{M_s}{M_\alpha} \frac{\langle \exp(-\beta U_{\text{intra}})\rangle}{\langle W \exp(-\beta[U_{\alpha,s} + U_{\text{intra}}])\rangle} \qquad (9)$$

Finally, it is important to point out that eqs 1, 6, 7, and 9 correspond to a canonical (NVT) ensemble. In this work, however, we have chosen to carry out the simulations of the polymer in an isobaric–isothermal (NPT) ensemble which allows for volume fluctuations. For such an ensemble, eq 9 is replaced by

$$H_w^{(\alpha)} = \frac{1}{\beta}\rho_s \frac{M_s}{M_\alpha} \frac{\langle V_s\rangle \langle \exp(-\beta U_{\text{intra}})\rangle}{\langle W V_s \exp(-\beta[U_{\alpha,s} + U_{\text{intra}}])\rangle} \qquad (10)$$

where V_s is the instantaneous volume of the simulated polymer matrix.

Simulation of the Polymer–Solute System. In a strict sense, Henry's law is only valid in the limit of infinite dilution. As the concentration of the solute rises, deviations from Henry's law can become important, depending on the nature of solute–polymer interactions. Solubilities must therefore be simulated by taking into account explicitly the presence of the solute in the polymer-rich phase. Further, given that many solutes of interest are fluids for which an analytical expression for the chemical potential is not available, the solute-rich phase (which can be gaseous or liquid) must also be simulated.

The simulation of solubility in a polymer is therefore carried out in the Gibbs ensemble. The main difficulty arising from the use of this ensemble in the context of long, articulated molecules is the required exchange of particles between coexisting phases. We have recently developed a method that, to some extent, overcomes this difficulty. Since in our original publication[7] the method was only applied to pure alkanes, we give here a brief discussion of the governing equation for mixtures.

Simulations are carried out in two boxes. The acceptance criteria for trial moves within each of these boxes are those pertaining to a canonical ensemble. The volumes of these boxes are allowed to fluctuate. The acceptance criteria for volume moves are those of a conventional Gibbs-ensemble simulation for a binary mixture at constant pressure.[11] Particle transfers from one box to the other are also permitted. In order to facilitate the insertion of an articulated molecule (e.g., an alkane) into a dense phase, the transfer is performed in a manner that is analogous to the insertion of test particles in simulations of the chemical potential. The transfer of a molecule of species α from box II into box I is accepted with probability

$$P_{\text{transfer}} = \min\left(1, \frac{W_{\text{old}}^{\text{I}}}{W_{\text{new}}^{\text{II}}} \exp\left(-\beta\left[\Delta U^{\text{I}} + \Delta U^{\text{II}} + \frac{1}{\beta}\ln\frac{V^{\text{II}}(N^{\text{I}}+1)}{V^{\text{I}}N^{\text{II}}}\right]\right)\right) \qquad (11)$$

where ΔU^{I} denotes the change to the potential energy of box I created by the insertion of the exchanged molecule and ΔU^{II} is the corresponding change in box II as a result of the removal of the exchanged molecule. The volume and number of particles in box I (before the attempted move) are denoted by V^{I} and N^{I}, respectively, and analogously for box II. The Rosenbluth weights for the transferred molecule before and after the trial move are denoted by $W_{\text{old}}^{\text{I}}$ and $W_{\text{new}}^{\text{II}}$, respectively.

Model and Simulations

Simulation of the Host Polymer Matrix. Here we are primarily interested in the solubility of intermediate-length alkanes in polyethylene. The first problem to address is therefore that of simulating pure polyethylene melts. We have recently developed a Monte Carlo scheme (CCB Monte Carlo) for efficient sampling of the phase space available to dense polymeric systems.[10] Using a combination of the CCB method and conventional reptation moves for the chains (about 50% of the total number of moves), we have generated equilibrium configurations for a system 10 polyethylene molecules of 71 interaction

Table I. Properties of Simulated Melts of C_{71}

T (K)	P (bar)	N^a	ρ (g/cm^3)	$\langle r^2\rangle^b$ (nm^2)	$\langle s^2\rangle^c$ (nm^2)
473	1	10	0.749 (11)	12.97 (155)	1.86 (16)
513	1	10	0.725 (10)	11.81 (140)	1.70 (15)

^{a} N = number of chains of 71 segments each. ^{b} $\langle r^2\rangle$ = mean-square end-to-end distance. ^{c} $\langle s^2\rangle$ = mean-square radius of gyration.

sites each in the *NPT* ensemble. These configurations were obtained over simulations of 10^7 Monte Carlo steps.

In our united-atom representation of polyethylene, each interaction site corresponds to a methylene or methyl group. Sites in different molecules and sites on the same molecule but separated by more than three bonds interact through a Lennard-Jones (LJ) 6–12 potential energy function. The Lennard-Jones parameters for interaction between sites are σ = 0.394 nm and ϵ = 0.410 kJ/mol. The simulations of the host polymer matrix (pure polymer) were carried out using the same interaction parameters for both central (CH_2) and chain-end (CH_3) groups. In addition to LJ interactions, a torsional potential energy function is imposed on rotations about carbon–carbon bonds. Additional details concerning these simulations can be found elsewhere.[3]

Simulation of Henry's Constants. One out of every thousand structures generated through our CCB simulations was stored for subsequent use in chemical potential calculations. As mentioned above, a test molecule is used to sample the potential energy surface of the polymer. The interaction parameters employed to describe the test particle's (lower alkanes) middle-chain segments (CH_2 groups) are identical to those used for the polymer; for chain-end segments (CH_3 groups), however, we use slightly different parameters. These are σ = 0.394 nm and ϵ = 0.750 kJ/mol; interactions between unlike pairs are computed via the usual Lorenz–Berthelot combining rules. These particular values for CH_3 groups were adjusted to give values for the density and the heat of vaporization of a simulated pure C_{11} system in agreement with experiment.

The averages required for calculation of the chemical potential were performed by attempting 25 000 test-molecule insertions on each of the stored polymer-matrix configurations.

Simulation of the Polymer–Solute System. Simulations of the polymer–solute system were carried out in the Gibbs ensemble. The initial configuration for the polymer phase was taken from our pure polymer simulations. Cycles of 1000 particle moves were carried out after every volume-change attempt and after every series of particle-transfer attempts. The number of particle-transfer attempts per cycle was adjusted so that not more than two or three particles were transferred.

Given the computational effort required for these calculations, we restricted our attention to systems of 10 polyethylene chains (of 71 segments) and 60 pentane chains. Finite-size effects are still important in this system. The aim of these initial studies, however, has been that of illustrating the methods that we have developed so far with applications to realistic fluids. We have therefore used a system size that is large enough to yield meaningful results but small enough to allow us to carry out simulations in the limits of available computing resources.

Results and Discussion

The characteristics of the simulated pure polymer melts are given in Table I. The density and configurational properties of these systems compare favorably with experiment. While the mean radius of gyration of the chains is smaller than half the edge of the simulation box, the difference between these two quantities is not too large (about 0.3 nm). Size effects are still noticeable in our simulations and better results could be obtained on larger systems, provided the computational resources are available.

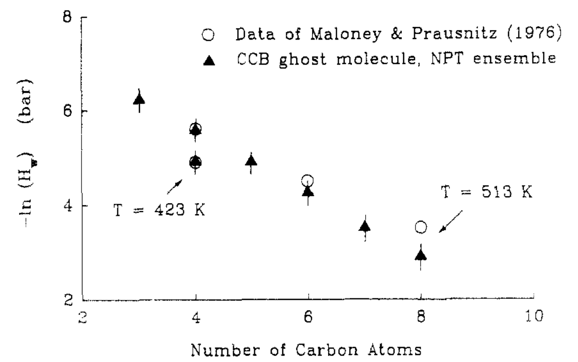

Figure 1. Simulated and experimental Henry's constants for linear alkanes dissolved in polyethylene at 1 bar and at two different temperatures.

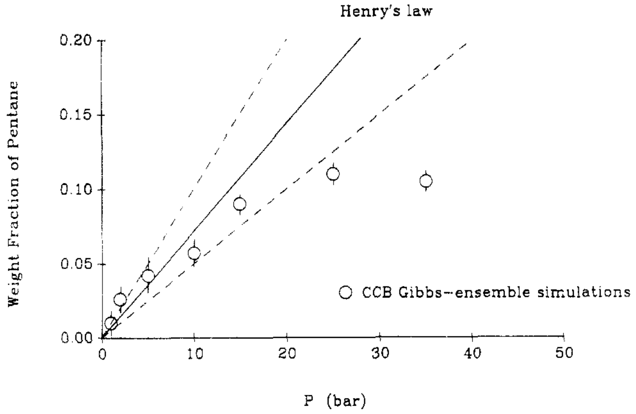

Figure 2. Solubility of pentane in polyethylene as a function of pressure at 513 K. The region between the dashed lines corresponds to the solubility calculated according to Henry's law (with its corresponding statistical uncertainty).

Figure 1 shows simulated and experimental Henry's constants for linear alkanes dissolved in polyethylene. Results are given for *n*-alkanes from propane to octane, at 1 bar and at two different temperatures. Agreement with experiment is satisfactory; the simulations give both the correct temperature and chain-length dependence for the chemical potential of the solute. Simulated Henry's constants could be further improved by small adjustments of the interaction parameters; such an effort, however, seems unwarranted given the large scatter of published experimental values. Further, larger systems should be simulated before better agreement with experiment is sought.

Figure 2 shows simulated results for the solubility of pentane in polyethylene at 513 K and at several pressures. The region between the dashed lines corresponds to the solubility calculated according to Henry's law (with its corresponding statistical uncertainty). At low pressures the results of Gibbs-ensemble and infinite-dilution simulations are consistent. At moderate pressures, however, deviations from Henry's law become significant. Finally, at pressures around 20 bar, the polymer reaches a saturation limit above which the solubility of pentane increases only marginally.

The density of the polymer (on a pentane-free basis) changes as a function of pressure, the dissolution of pentane leading to a swelling of the polymer matrix. This swelling is accompanied by an increase of the end-to-end distance of the chains. In order to characterize the polymer swelling

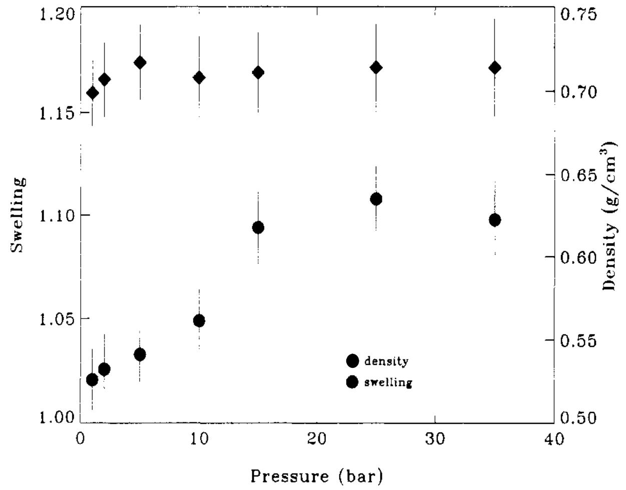

Figure 3. Density (filled diamonds) and swelling (filled circles) of polyethylene saturated with pentane at 513 K as a function of pressure. The swelling is defined as the ratio of the volume of a given amount of polymer saturated with pentane at a given pressure to the volume of the same amount of pure polymer.

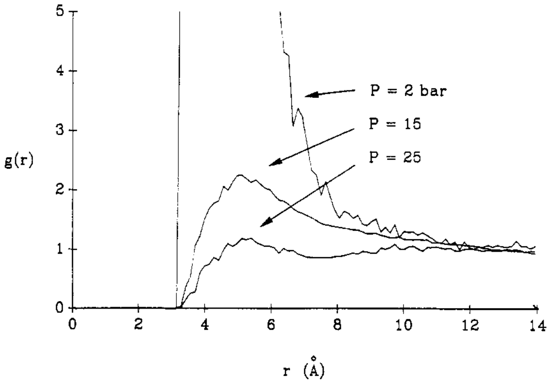

Figure 4. Radial distribution functions (rdf) for pentane–pentane interaction sites at P = 2, 15, and 25 bar.

at a given pressure quantitatively, we plot in Figure 3 the ratio of the volume of a given amount of polymer saturated with pentane at a given pressure to the volume of the same amount of pure polymer (filled circles). Additionally we plot on the same figure the density of the polymer saturated with pentane as a function of pressure (filled diamonds). Within the statistical uncertainty of the simulation, the density remains virtually constant as the pressure is increased and, as a consequence, the pressure dependence of the swelling is identical to that of the solubility (Figure 2).

Figure 4 gives radial distribution functions for pentane–pentane interaction sites at several pressures. At low pressures (2 bar), the simulated rdf exhibits a pronounced sharp first peak which indicates that dissolved pentane molecules have a strong tendency to form dimers and trimers. Note, however, that the statistical uncertainty associated with this distribution function is large due to the fact that the required averaging has been performed over a relatively low number of molecules. The rdf gives the probability of finding two pentane molecules at a distance r apart relative to a uniform distribution; the appearance of just a few dimers is therefore enough to drive the first peak well above a value of unity. Nonetheless, a visual analysis of the polymer–solute system indicates that a low pressures solubility occurs primarily in "pockets" where two or three pentane molecules fit tightly together. For higher pentane concentrations, this tendency disappears and, as the rdf's indicate, the solute is almost uniformly distributed in the polymer.

Two shortcomings of the Gibbs-ensemble methodology, as implemented here, should be pointed out. The first is that the response of the polymer to the presence of the solute is relatively slow. The nature of CCB polymer moves is such that segments near the ends move more often than segments in the middle of a chain.[10] These simulations therefore require a large number of simulation steps, and the statistical uncertainty of the results is large. This problem could be overcome by combining CCB polymer moves and other, more localized types of moves such as the "concerted rotations" proposed recently.[12,13]

A second shortcoming of the particle-insertion methods discussed here is that there is a limit to the size of the solutes that can be studied (on the order of 20 segments, for linear alkanes). For longer chains, a combination of these methods and other, different approaches (such as the ghost-segment method of Kumar et al.[11]) might prove to be useful. Calculations of the solubility of a large solute in a polymer, however, would require simulation of much larger systems and substantial computational resources.

Conclusions

New methods for simulation of phase equilibria for systems of long, articulated molecules have been developed. We have applied these methods to the calculation of Henry's constants and solubilities of linear alkanes in polyethylene. To the best of our knowledge, these are the first simulations aimed at computing the solubility of realistic, flexible molecules in a polymer. Comparison of the methods' efficiency and quality of results to those of previous simulations has therefore not been possible. Agreement with experiment, however, is satisfactory.

In this first investigation we have limited our attention to the study of oversimplified model alkanes and polyethylene. One of the main purposes of our work, however, has been that of developing simulation methods that will eventually yield meaningful predictions of solubility in polymers; their usefulness will only be assessed after studying more realistic molecular models.

Acknowledgment. The authors are grateful to L. Dodd and D. Theodorou for very fruitful discussions. Generous grants of computer time on the NEC SX-3 of the CSCS (Centro Svizzero di Calcolo Scientifico) in Manno and on the Cray Y-MP/464 of ETH Zürich are gratefully acknowledged.

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