Molecular Simulation of the Pure *n*-Hexadecane Vapor−Liquid Equilibria at Elevated Temperature

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Introduction

The accurate knowledge of the phase behavior of polymer solutions is especially important for polymer production, separation, and purification processes. Computer simulation has proven a valuable tool for this type of calculation. However, traditional techniques (grand canonical and Gibbs ensemble[1] Monte Carlo simulation) developed for simulating systems of small molecules fail when applied to polymers. These techniques involve the insertion or transfer of a molecule, and the success of these attempted moves becomes highly improbable when the system considered is dense and the molecules are long, as is the case in polymer systems.

Recent developments for long alkane systems utilize the NPT-μ method[2−4] in order to calculate their phase envelope. The method is based on the equalization of the chemical potentials of the species involved. The liquid and the gas phases are simulated separately and Widom insertions[5] are conducted in both phases. The incremental ansatz[6] is usually invoked in order to facilitate the above calculations. The potential models that are used vary from fully flexible (idealized) to semiflexible (realistic) models. Smit et al.[7] calculated the phase envelope of pure alkanes up to *n*-C_{48} by using configurational bias Gibbs ensemble techniques with a realistic potential model representation.

In this work, the phase envelope of pure *n*-hexadecane is calculated by an iterative scheme, similar to that used in the NPT-μ method. The scheme involves the simultaneous simulation of two distinct phases in the NPT ensemble. The chemical potentials are calculated in both phases and their equalization controls the convergence of the scheme to the saturation pressure. Insertions of test hexane molecules and virtual augmentations of hexadecane chains by one segment, carried out with a configurational bias Monte Carlo algorithm, in combination with the chain increment ansatz, are used in order to estimate efficiently the chemical potential of *n*-hexadecane. It has been proven elsewhere[8] that this is an accurate and computationally efficient way to estimate the chemical potential of the long chains. The excess chemical potential of the oligomers and the excess segmental chemical potential are calculated using an exact mathematical formulation given therein.[8] Chains in this work are simulated with a united atom model,[9] suitable for realistic representation of long chain systems.

Simulation Details

The potential model used in this work is the one given by Dodd and Theodorou[9] and has been tested successfully for *PVT* and structural properties in both gas and liquid phases of pure hexadecane.[8,9] It is a united atom model that uses the Lennard-Jones potential to account for nonbonded inter- and intramolecular interactions. Methylene and methyl groups are treated with the same energetic and size parameters. The torsional potential of Ryckaert and Bellemans is applied, while the bond lengths and the bond angles are kept fixed. The analytic description and the parameters of the model can be found elsewhere.[8]

To locate a vapor−liquid coexistence point, two phases are simulated independently at constant, common temperature and pressure (NPT ensemble). The liquid and the vapor phases used here consist of 32 and 16 chains, respectively. An initial pressure, on the order of the experimental vapor pressure for the set temperature, is chosen. After equilibrating at this pressure, a new, improved pressure is estimated according to the following equation:

$$\Delta P = -\lambda \frac{\mu^{\mathrm{liq}}(T,P) - \mu^{\mathrm{vap}}(T,P)}{V^{\mathrm{liq}} - V^{\mathrm{vap}}} \qquad (1)$$

where V symbolizes volume per molecule and μ the molecular chemical potential. The prefactor λ ($0 < \lambda \leq 1$) in eq 1 can be used optionally in order to limit the change in pressure when the chemical potentials of the component in the two phases differ appreciably. The total chemical potentials appearing in the numerator of eq 1 are evaluated from the excess chemical potentials by adding the ideal gas contribution:

$$\mu^{\mathrm{liq}}(T,P) - \mu^{\mathrm{vap}}(T,P) = \mu^{\mathrm{ex,liq}}(T,P) - \mu^{\mathrm{ex,vap}}(T,P) + k_{\mathrm{B}}\mathrm{T} \ln \frac{\rho^{\mathrm{liq}}}{\rho^{\mathrm{vap}}} \qquad (2)$$

with ρ the molecular density. The excess chemical potential in each phase is estimated by conducting Widom insertions of an oligomer (*n*-hexane) and by incrementing a randomly selected existing *n*-C_{16} chain by one end segment. Both the test oligomer insertion and virtual augmentation process are conducted with a configurational bias Monte Carlo integration scheme. The incremental ansatz is invoked to estimate μ^{ex} from the excess hexane and segmental chemical potentials. This has proven to be an accurate and easy way to calculate chemical potentials of realistic models of long hydrocarbons.[8] The full mathematical formulation and simulation details can be found elsewhere,[8] and are not repeated here.

Results and Discussion

The simulation data for the phase envelope of pure *n*-hexadecane are presented in Table 1. They are also plotted against the Lee−Kessler[10] correlation predictions, which are practically indistinguishable from

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Table 1. Phase Coexistence for Pure *n*-Hexadecane

	P^{sat} (atm)		ρ^{liq} (g/cm^3)		ρ^{vap}(g/cm^3)	
T (K)	expt	simul	expt	simul	expt	simul
550	0.788	1.47 ± 0.04	0.565	0.566 ± 0.032	0.0042	0.0081 ± 0.0024
580	1.485	2.5 ± 0.1	0.538	0.528 ± 0.034	0.0079	0.0135 ± 0.0041
610	2.595	4.4 ± 0.2	0.510	0.501 ± 0.040	0.0140	0.0230 ± 0.0072
650	4.994	6.9 ± 0.2	0.465	0.431 ± 0.050	0.0285	0.0380 ± 0.0124

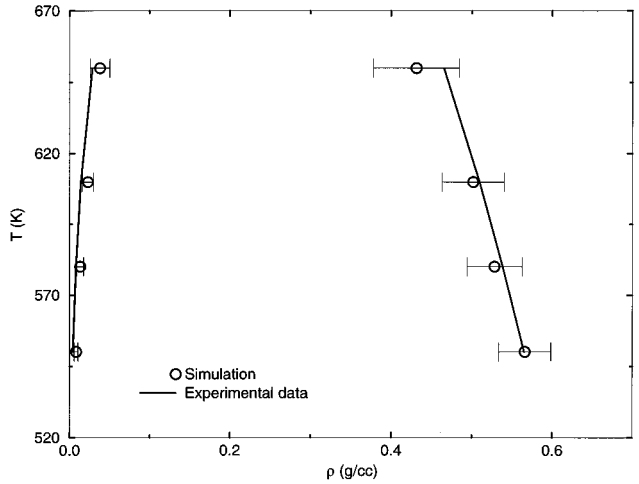

Figure 1. Phase envelope of pure *n*-hexadecane.

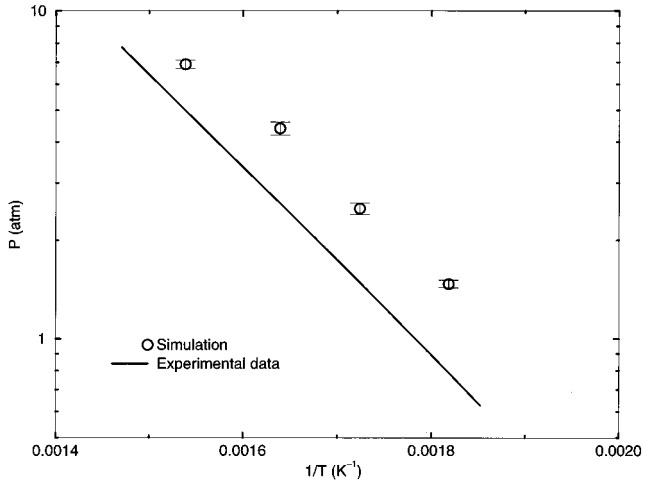

Figure 2. Saturated pressure as a function of temperature for pure *n*-hexadecane.

experiment for this system, in Figure 1. The agreement is fairly good. The large error bars in density result from (a) the small number of molecules used, especially in the gas phase, (b) the range of low pressures simulated (1−8 atm), which is notoriously difficult to capture precisely in the NPT ensemble, and (c) the relative proximity to the critical point. The predicted saturated pressure at the temperatures studied is given in Table 1 and Figure 2. Reported errors on P^{sat} are based on the ΔP values imposed in the last iteration of the scheme. Experimental data are also shown for comparison.[10] As the temperature increases, the agreement between simulation and experimental data for P^{sat} improves.

The critical properties were estimated by fitting the predicted liquid and vapor densities to the rectilinear diameter rule and to the scaling relationship for the width of the coexistence curve,

$$\frac{\rho_{liq} + \rho_{vap}}{2} = \rho_c + A(T - T_c) \quad (3)$$

$$\rho_{liq} - \rho_{vap} = B(T - T_c)^{\beta} \quad (4)$$

where β is the critical exponent, taken equal to an Ising-type critical exponent ($\beta = 0.32$). Thus, the estimated critical properties are $T_c = 700 \pm 10$ K ($T_{c,exp} = 723$ K), $\rho_c = 0.21 \pm 0.03$ g/cm^3 ($\rho_{c,exp} = 0.219$ g/cm^3). The critical pressure was estimated by a simple linear extrapolation, resulting in $P_c = 13.4 \pm 1.6$ atm ($P_{c,exp} = 13.8$ atm, Figure 2). Experimental critical values are taken from ref 11.

Deviations between simulation and experiment are due to the fact that the interaction potential employed in the simulation is not perfect. Nevertheless, one can conclude that the iterative two-phase simulation scheme proposed herein, taking advantage of the chain increment ansatz, is useful for estimating the phase equilibrium properties of chain liquids with modest computational cost. On the basis of preliminary calculations, the CPU time needed for a phase equilibrium calculation, at a temperature well below the critical temperature of pure *n*-hexadecane, with the scheme utilized in this work, is on the order of 20−50% lower than the corresponding CPU time using the Gibbs ensemble approach. This ratio becomes progressively lower for longer *n*-alkanes.

References and Notes

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