

An Improved Gibbs Ensemble-Monte Carlo Method for Phase Equilibria Calculations in Polymer Mixtures

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Summary

In the present work, an extension of the Gibbs Ensemble-Monte Carlo method is proposed for phase equilibria calculations in polymer systems. The new method makes use of cell lists, a technique widely used in conventional molecular dynamics, to handle the special computational requirements of the algorithm. The new method is found to scale roughly with the number of interaction centers, N , which presents a huge improvement over the original Gibbs-Ensemble method. The gain in computer time can be as large as 10 times or even larger. This fact allows us to consider longer time and length scales. Simulation results on phase equilibrium diagrams of long-alkanes and their mixtures with smaller molecules are reported. Moreover, simulation results are presented on the solubility of small molecules in amorphous polyethylene.

Introduction

The phase behavior of fluids and their mixtures is of great importance to many scientific disciplines. In polymerization engineering, the phase behavior of the system is critical for the accurate design and simulation of polymerization processes. The experimental determination of a multi-

component phase diagram, however, is a costly procedure, which is often restricted to a narrow range of temperature, pressure and compositions. The use of various equation of state models is also based on the availability of suitable experimental data, and usually their predictive capability is limited.

In recent years, the use of molecular simulations has received considerable attention as an alternative approach for predicting the phase equilibrium behavior of fluids. Several molecular simulation methods have been proposed to calculate the phase equilibrium behavior of polymer-solvent systems. In the present study the Gibbs Ensemble Monte-Carlo method is considered. It provides a direct and computationally efficient way for the study of phase coexistence properties of various fluids and their mixtures. The method applies to polymer mixtures as well but certain modifications are needed in order to effectively handle the increased number of interaction centers involved. Thus, advanced techniques have been developed to account for polymer chain relaxation. However, they are usually restricted to polymers of relatively small molecular weight since the time needed for such simulations is proportional to the square of the number of interaction centers, N^2 . The new method, proposed in the present study, addresses the problem of reducing the simulation time. It is shown that, in most cases, the method succeeds in achieving a simulation time that is proportional to N .

The New Simulation Method

The Gibbs Ensemble Monte-Carlo method has been extensively used for predicting phase equilibrium properties of many different substances. The original scheme [1] introduces two thermodynamically coupled boxes, one representing the gas phase and the other the liquid phase. The molecules of the substances to be simulated are randomly inserted in each box. These two systems can exchange molecules and volume. Three basic types of trial moves are considered: displacement of a randomly selected molecule, variation of the volume, so that the total volume remains constant, and exchange of molecules between boxes. These moves ensure equation of temperature, pressure and chemical potential

in both boxes. A detailed description of the method together with the acceptance rules can be found in reference [2].

When considering polymer chains in the simulation, new moves have to be introduced in order to take into account the topological constraints and relaxation of the polymer chains. We have used both configurational-bias [3] and recoil-growth [4] techniques in order to modify the internal conformation of a polymer chain, as well as translation of the center-of-mass and rotation of the chain around its center-of-mass.

The molecules interact with each other via an intermolecular potential, which is usually of the Lennard-Jones or Buckingham type, and via their electric charges, provided the molecules bear non-zero dipole moments. There are many such potentials reported in the literature, which have been developed specifically for this type of calculations. Moreover, when long chain molecules are introduced, intra-molecular potentials are also taken into account.

The largest portion of the computer time in a Gibbs Ensemble simulation is spent on calculating the interaction energies between the molecules in a box. Thus, for every trial move attempted, the interaction energy between the chosen molecule and all the other molecules in the box needs to be evaluated. This means that, if no special techniques are employed, due to the pair-wise additive interactions, the time needed to compute this energy scales with the square of the number of interaction centers, N^2 . A number of techniques, including Verlet lists, cell lists or a combination of both [2], have been developed for conventional Monte-Carlo and molecular dynamics algorithms to reduce the computational time. However, these techniques have not been applied until now to the Gibbs Ensemble method for two main reasons. First, the number of interaction centers considered, was usually small and, second, the original Gibbs-Ensemble method needs to be properly modified. In this work, we apply the cell list technique to the classical Gibbs-Ensemble method. The two simulation boxes are divided in a number of cubic cells. The linear dimension of these cells is chosen so that it is larger than the cut-off distance of the potential, and they exactly cover the simulation box.

In this way, an atom interacts with those atoms in the same cell and the 27 neighboring cells. Notice that the cell size is in general different in the two boxes. Most of the moves can be straightly modified in order to use cell lists. The volume variation move though, which modifies the dimensions of a simulation box, requires some special treatment. In fact, rearrangements of all the particles in the cells together with a cell length change in the box are necessary. This means that the number of cells in a box is not constant throughout the simulation and may vary with time as the volume of the box changes.

Simulation Results

The above method proved to be very efficient when it was applied to a broad range of different vapor-liquid phase equilibrium problems. The gain in CPU time was of the order of 2 to 15 times for small molecules (e.g., CO₂, H₂O, C₂H₄, etc.) depending on the system size. In general, for larger system sizes the gain in the CPU time was higher.

The computational efficiency of the algorithm was more pronounced in the case of long chain molecules. Figure 1 depicts the achieved reduction in CPU time by the new method in terms of number of tetracontane molecules in the system. The tetracontane molecules were interacting via the TraPPE force field [5]. Since each tetracontane molecule comprises 40 interaction groups, the maximum number of interacting beads in the system was $N=40000$, which was easily handled by the new method. On the other hand, the conventional Gibbs-Ensemble method required a prohibitively long time (roughly 60 times more) when using the straightforward energy calculation. It is apparent that the new method scales roughly with N , in contrast to the N^2 dependence of the conventional method. It is also important to mention that the results obtained by the two methods are identical since, in practice, the new method simply rejects the calculation of interactions that do not contribute anything to the final result.

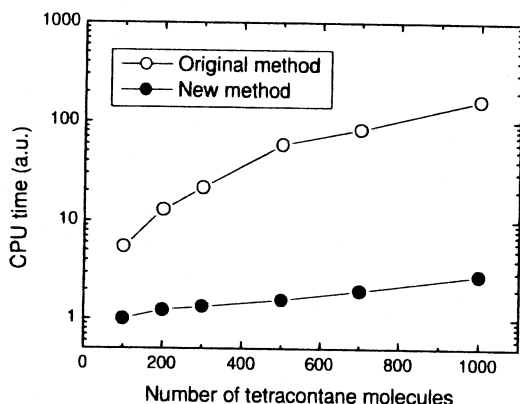


Figure 1: Comparison of the CPU times (in arbitrary units) required by the original and modified Gibbs-Ensemble methods as a function of the number of alkane molecules in the system.

We applied the same technique for the calculation of the vapor-liquid coexistence curves of different alkane chains. In Figure 2, the calculated vapor-liquid coexistence curves (denoted by the discrete points) are compared with experimental measurements (e.g., continuous lines). It can be seen that there is an excellent agreement between experimental data and simulation results. It is apparent that we can easily predict the vapor-liquid coexistence curve of alkane chains comprising as many as 60 groups each. Moreover, the simulations provide a wealth of information regarding critical points, critical temperatures, vapor pressures, etc.

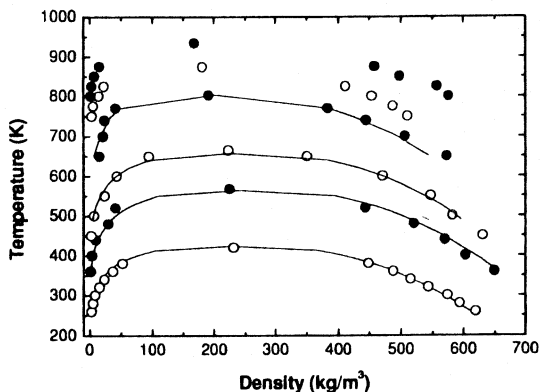


Figure 2: Vapor-liquid coexistence curves (from bottom to top): butane, octane, dodecane, tetracontane, tetracontane, and hexacontane.

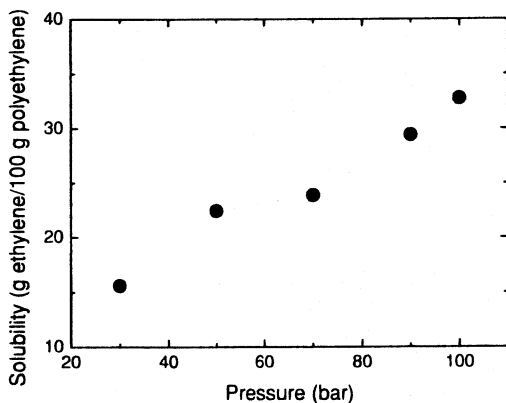


Figure 3: Solubility of ethylene in amorphous polyethylene at 25 °C using the Gibbs Ensemble method

In Figure 3 the calculated solubility of ethylene in amorphous polyethylene at 25 °C is plotted with respect to pressure. The new algorithm reduced the total simulation time by a factor of 5 to 10. Notice that the simulation results are similar to those of reference [6] and compare quite

well to available experimental data. The method has also been applied to systems of three or more components, and according to our preliminary results, appears to be very efficient.

Literature References

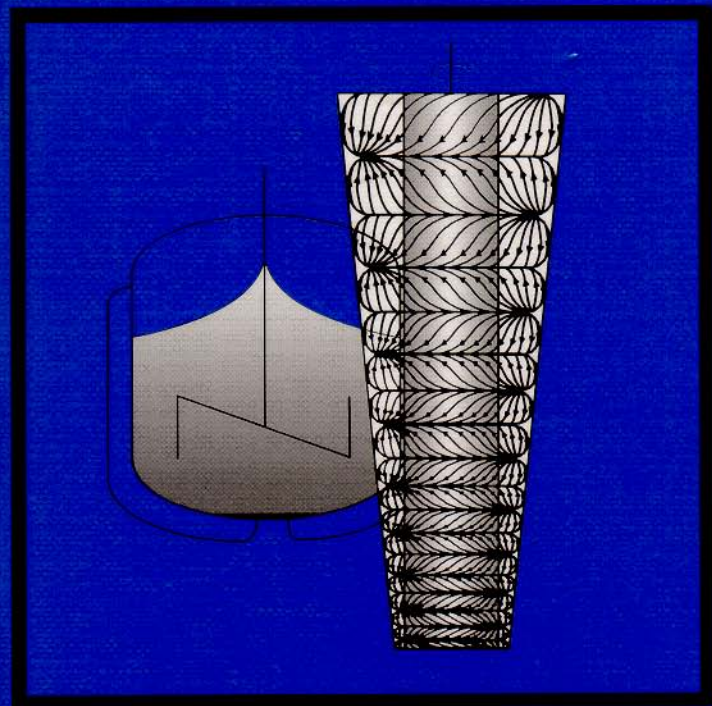
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