LETTER TO THE EDITOR

Direct simulation of phase equilibria of chain molecules

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Abstract. We show how to combine a novel Monte Carlo scheme to sample conformations of chain molecules with the Gibbs-ensemble method to simulate fluid–fluid phase coexistence. This approach allows us to compute liquid–vapour equilibria in chain molecules containing 8–15 monomers. As an example, we report the first simulation of the vapour–liquid coexistence curve of an eight-bead Lennard-Jones molecule.

One of the most important applications of computer simulations of classical fluids is the direct calculation of phase diagrams. In particular, having the facility to compute the fluid–fluid coexistence curve of an arbitrary model for an atomic or molecular fluid, or fluid mixture, is of considerable practical importance. However, until recently, the numerical study of liquid–vapour phase equilibria was an arduous task, even for the simplest (i.e. atomic) systems. This state of affairs changed completely with the introduction by Panagiotopoulos and co-workers of the so-called Gibbs-ensemble Monte Carlo (GEMC) scheme [1–3]. Using this method, fluid–fluid equilibria in atomic, or simple molecular, systems can be simulated directly using a relatively small number of particles. In fact, since the introduction of the GEMC method, a very large number of numerical studies of liquid–vapour phase equilibria have been reported. However, these simulations are all limited to model systems containing atoms or small molecules. The reason for this becomes clear if we recall that one of the steps in the GEMC scheme involves the random insertion of particles in a fluid. Using the conventional (random) sampling schemes, successful insertions can only be achieved for small molecules. At typical liquid densities the probability of the successful insertion of a monomer is of the order of 0.5%, the probability of inserting a chain of eight of these monomers is less than 10^{-18}. Such a low probability of insertion would necessitate billions of years of computer time to compute a coexistence curve. In this letter, we present an extension of the GEMC method that makes it possible to perform direct simulations of phase equilibria involving chain molecules. This is of considerable interest for two reasons: first of all, from a fundamental point of view, there is a scarcity of 'hard' data that allow us to test theories of liquid–vapour phase coexistence in poly-atomic fluids. Secondly, the practical importance of numerical simulations of phase equilibria involving (mixtures of) truly poly-atomic molecules far transcends that of the study of phase equilibria involving atoms or small molecules. In what follows, we briefly recall the essentials of the GEMC method. Next, we sketch our extensions to this scheme, which make it

possible to study phase equilibria involving flexible, poly-atomic molecules. Finally, as an example, we report the observation of liquid–vapour phase separation in a system of 'Lennard-Jones'-chain molecules of eight monomeric units.

In GEMC simulations, one studies the equilibrium behaviour of a system of N particles, with a total volume V at a temperature T. This system is divided into two (periodic) sub-systems, which can exchange both volume and particles. When the system as a whole is at a state point in the two-phase region, the state of lowest free energy is one in which one box contains bulk vapour and the other the bulk liquid. Since the two boxes are not in direct contact, this equilibrium is achieved without the presence of an interface. It is precisely the absence of such an interface that makes it possible to obtain information about coexistence between bulk phases from a single simulation.

In a GEMC simulation, three types of trial move can be performed:

(i) Random displacement of a particle inside either box,

(ii) random change of the volume of both boxes in such a way that the total volume remains constant, and

(iii) exchange of particles between the two boxes.

It is the last step that has a prohibitively low acceptance for chain molecules, since a random insertion of a poly-atomic molecule in a fluid will almost always result in an overlap with one of the other chains. Below, we describe a novel algorithm that allows us to bias the insertion of chains in such a way that the 'holes' in the system are found. This method of insertion would bias the simulations if the ordinary acceptance rules were used. Here we show that the correct distribution of configurations can be sampled if the acceptance rule for this step is modified. Our approach is based on a 'configurational-bias' Monte Carlo scheme for continuously deformable molecules which we described in an earlier publication [4].

Consider a trial move to remove a molecule from one box (say, 1) and insert it in the other box (2). To achieve this, we first insert a chain molecule in box 2, using a stepwise method. First, we attempt to insert a single monomer in box 2. Next, k random trial segments are generated, such that the next monomeric unit is located somewhere on a spherical shell around the first monomer. For each of these trial segments, the potential energy due to interaction with the other particles in the system is calculated and one of the directions, say direction i, is selected with a probability given by

$$P_2(n) = \frac{\exp[-\beta u_2(i)]}{\sum_{j=1}^{k} \exp[-\beta u_2(j)]} \tag{1}$$

where $\beta = 1/k_B T$ and $u(j)$ is the energy of a jth trial direction and n labels the position of the segment in the chain. The subscript (in this case 2) indicates the box in which these quantities are calculated. In addition, we compute a weight factor

$$W_2(n) = \left(\sum_{j=1}^{k} \exp[-\beta u_2(j)] \right) W_2(n-1). \tag{2}$$

$W_2(0)$, the weight factor for the monomer, is simply the Boltzmann factor associated with the random insertion of a monomer. At the same time we calculate a corresponding weight factor $W_1(n)$ for the chain that we chose to remove from box 1

$$W_1(n) = \left(\sum_{j=1}^{k} \exp[-\beta u_1(j)] \right) W_1(n-1) \tag{3}$$

where the summation is over the same set of trial directions as in box 2 with the restriction that the orientation selected in box 2 is replaced by the actual orientation of the chain in box 1 of that particular segment. This procedure is repeated until the chain has the desired length ($n = l$).

In the original scheme described in [4], the overall acceptance probability of such a trial move would be $\min(1, W_2(l)/W_1(l))$. Using this method, it is possible to study chain molecules of 10–30 beads in a moderately dense liquid [4, 5].

In order to use this method to move molecules from one box to the other in a GEMC simulation, we should use a slightly different expression for the acceptance probability of trial moves. To this end, we impose detailed balance on our Monte Carlo procedure. This implies that, in equilibrium, the rate at which particles are moved from box 1 to 2 equals the reverse rate:

$$N(1)P(1|2)\mathrm{acc}(1|2) = N(2)P(2|1)\mathrm{acc}(2|1) \tag{4}$$

where $N(1)$ is statistical weight of the initial configuration with n_1 chains in box 1 with volume V_1, and $n_2 \equiv N - n_1$ particles in box 2 with volume $V_2 \equiv V - V_1$. $P(1|2)$ is the probability that, starting from the current configuration, a configuration 2 is generated with $n_1 - 1$ particles in box 1 and $n_2 + 1$ in box 2. $\mathrm{acc}(1|2)$ denotes the probability this trial move is accepted. The ratio of the statistical weights $N(1)$ and $N(2)$, is given by

$$\frac{N(1)}{N(2)} = \frac{V_1^{n_1} V_2^{n_2} (n_1 - 1)!(n_2 + 1)! \exp[-\beta U(1)]}{V_1^{n_1-1} V_2^{n_2+1} (n_1)!(n_2)! \exp[-\beta U(2)]} \tag{5}$$

where $U(1)$ ($U(2)$) is the total potential energy of configuration 1(2).

Substituting these equations into (4), using equations (1)–(3), we find that the following acceptance rule for the exchange step will satisfy the detailed balance condition

$$\mathrm{acc}(1|2) = \min\left(1, \frac{n_1(V - V_1)}{(N - n_1 + 1)V_1}\frac{W_2}{W_1}\right). \tag{6}$$

This demonstrates that we can use the biased insertion and still sample the correct distribution of configurations provided we use the acceptance rules given by (6). At this stage, it is worthwhile pointing out that, with trivial extensions, the above scheme can be applied to mixtures of chain molecules.

As an illustration of the scheme described above, we consider a model system containing 200 chain molecules consisting of eight 'monomers' connected by bonds of a fixed length σ. The bonds are allowed to rotate freely with respect to each other. The monomer–monomer interaction is modelled by a Lennard-Jones potential that is cut off at a radius $R_c = 2.5\sigma$ and shifted:

$$V_{\mathrm{LJ}}^s(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] - V_{\mathrm{LJ}}(R_c). \tag{7}$$

Figure 1 shows the main result of our GEMC simulation, namely the liquid–vapour coexistence curve of this model system. In table 1, we have listed the densities of the coexisting phases as a function of temperature. In order to estimate the location of the liquid–vapour critical point, we have assumed the law of rectilinear diameters [6].
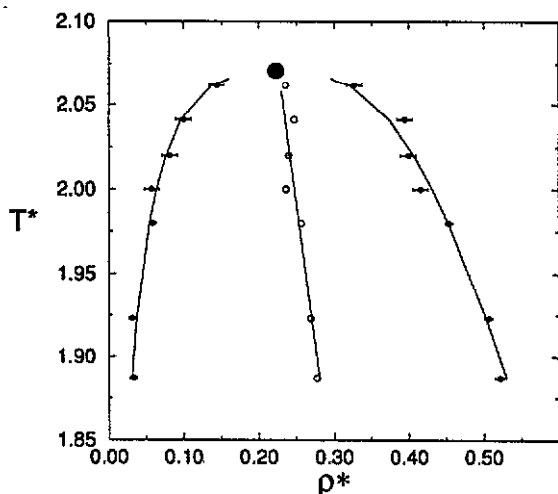
Figure 1. Liquid–vapour coexistence curve of a system of 200 chains of eight Lennard-Jones monomers as measured in our GEMC simulations. $T^* = kT/\epsilon$ and $\rho^* = \rho/\sigma^3$. Our estimate of the critical point is indicated by a black dot.

Indeed, we find that, in the temperature range studied, the means of the liquid and the gas densities fall on a straight line. Moreover, we assumed that, in the vicinity of the critical point, the shape of the coexistence curve is given by the scaling form

$$\rho_l - \rho_g = B(T - T_c)^\beta \qquad (8)$$

with the critical exponent $\beta = 0.32$†. Combining these two fits we arrive at an estimate of the critical point $T_c = 2.07$ and $\rho_c = 0.22$. This point is indicated by the black dot in figure 1. The phase diagram of *atoms* with an interaction potential given by equation (7) has been computed by Smit [7]. Comparing the two phase diagrams, one finds that the critical temperature for the chains is almost twice as high as for the atomic fluid and that the critical density is somewhat lower. Such behaviour is in qualitative agreement with the predictions of the Flory–Huggins theory and is also found experimentally [8]. A more detailed analysis of our simulation results will be reported elsewhere [9].

In summary, the technique described in this letter allows us to study the liquid–vapour phase coexistence of flexible, poly-atomic molecules. The same technique can also be used to study the phase behaviour of mixtures of different chain molecules, or chain molecules in a solvent. Although the results presented in this letter were limited to a chain consisting of eight monomeric units, preliminary results indicated that the method should work for chains with 8–15 beads. In fact, as the critical density for liquid–vapour phase separation is expected to decrease as $l^{-1/2}$ with increasing chain length, it seems likely that the GEMC technique may be used to estimate the critical point, even for chains that are rather longer than 15 units. We should stress that a Lennard-Jones chain of l 'monomers' separated by bonds of length σ is, in fact, appreciably longer than, say, a hydrocarbon molecule with the same number

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† If we use the classical exponent $\beta = 0.5$, rather than $\beta = 0.32$, our estimate for the critical temperature increases by no more than 1%.

Table 1. Temperature dependence of the densities of the coexisting liquid (ρ_l) and vapour (ρ_g) phases of a system of 200 eight-monomer Lennard-Jones chain molecules. Temperature and densities are in reduced units, $T^* = kT/\epsilon$ and $\rho^* = \rho/\sigma^3$. The error in the densities is given by the subscripts: e.g. 0.033_5 means 0.033 ± 0.005.

T^*	ρ_g^*	ρ_l^*
1.887	0.033_5	0.521_6
1.923	0.031_5	0.506_5
1.980	0.058_4	0.453_5
2.000	0.06_1	0.42_1
2.020	0.08_1	0.40_1
2.041	0.10_2	0.40_1
2.062	0.14_1	0.33_1

of monomers. For realistic models, the monomer–monomer distance is considerably less than the diameter of the monomers. We therefore expect that the technique described in this letter will allow us to study the phase behaviour of alkanes with up to 25 carbon atoms.

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