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Development of kinetic Monte Carlo and Bin-Monte Carlo schemes for simulation of mixtures – vapor–liquid equilibria & adsorption

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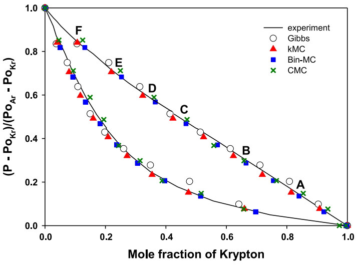
HIGHLIGHTS

- Bin-MC and kMC describe density profiles across vapour–liquid interface better than conventional Monte Carlo methods.
- Bin-MC and kMC yield excellent descriptions of phase equilibria and thermodynamic properties.
- kMC outperforms other MC methods in the determination of chemical potential.

GRAPHICAL ABSTRACT



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ABSTRACT

We describe algorithms for the recently developed Bin-Monte Carlo (Bin-MC) method (Fan et al., 2012) and kinetic Monte Carlo (kMC) (Ustinov and Do, 2012) to simulate binary liquid mixtures, and compare them with simulations of vapour–liquid equilibria from the canonical and Gibbs MC methods. We have found that in kMC, the rule to choose a molecule to move rests purely on the mobility, irrespective of molecular weight. In the Bin-MC, the choice of a molecule to move from one bin to another bin depends on the selection of a component with equal probability. Our simulations show that the Bin-MC and kMC schemes are very effective for the purpose of describing thermodynamic properties and density profiles across the vapour–liquid interface, and show that the Lorentz–Berthelot (LB) mixing rule works well for subcritical systems, and to improve the description of systems having one component under supercritical condition the cross collision diameter and the cross well depth have to be modified from the LB mixing rules, which is in agreement with previous studies (for example, (Wu and Sadus, 2000)). The benefits of the kMC scheme for the direct determination of chemical potential were also demonstrated with a study of adsorption of an argon–krypton mixture on graphite.

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1. Introduction

Monte Carlo (MC) simulations in the various thermodynamic ensembles have been widely used to describe many physical processes with great success and are conventionally effected via the Metropolis algorithm (Allen and Tildesley, 1989; Frenkel and Smit, 1996; Theodorou, 2010). In particular, phase equilibria are studied in the canonical or Gibbs ensembles (Carrero-Mantilla and Llano-Restrepo, 2003a, 2003b; Gao et al., 1997; Jin and Wang, 2000; Gotlib and Piotrovskaya, 1999; Gotlib et al., 1997).

When vapour–liquid equilibrium (VLE), with two contingent phases, is studied the density distribution is non-uniform across the interface separating the dense liquid phase and the rarefied gaseous phase. Sampling of the gaseous phase in this type of system,

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using conventional MC, is generally poor, since the displacement length must be chosen as a small fraction of the collision diameter to ensure efficient sampling in the dense regions. Small displacement lengths might also lead to a significant correlation between consecutive states and hence to a slow exploration of the phase space (Ustinov and Do, 2012). The Bin-MC scheme, recently introduced by Fan et al. (2012), overcomes these difficulties by taking advantage of the grand canonical features built within a canonical ensemble, to provide effective sampling of both dense and rarefied regions. A second novel technique originating from this group (Ustinov and Do, 2012; Nguyen et al., 2012; Fan et al., 2013a, 2013b), the kMC scheme, gives good results for phase equilibria and adsorption of pure components, because it offers a distinct advantage over other schemes in the direct determination of chemical potential. The statistical thermodynamic basis of the determination of the chemical potential in the kMC is established in our recent paper (Fan et al., 2013b). These two new methods, Bin-MC and kMC, have advantages over the classical Gibbs ensemble MC (GEMC) because they can describe density profiles across the vapour–liquid interface and determine the surface tension which cannot be obtained by the Gibbs ensemble because of the absence of interface in GEMC. Furthermore it is extremely difficult to calculate reliable thermodynamic properties at low temperatures in GEMC simulations due to the difficulty of inserting a particle into the dense phase.

Bin-MC has been successfully applied to *VLE*/*VSE* and adsorption of pure components (Fan et al., 2012). The kinetic Monte Carlo (kMC*)* method has been used to study *VLE* and adsorption of single components, such as argon and nitrogen with great success (Ustinov and Do, 2012; Nguyen et al., 2012; Fan et al., 2013a).

The kMC and Bin-MC schemes have been shown to work well for pure components, however it does not follow that they would necessarily work for mixtures. The purpose of this paper is to develop an algorithm for the kMC and Bin-MC methods that can be applied to the study of *VLE* in mixtures. The performance of the new algorithm is then compared with results obtained from the conventional canonical and Gibbs ensemble MC simulations and with the experimental data. We have also applied the kMC scheme to the study of mixture adsorption of simple gases on a graphite surface to demonstrate its advantage in the determination of chemical potential.

2. Theory

2.1. kMC in the canonical ensemble

Consider a canonical (N,V,T) ensemble comprising a total of N molecules and N_C components containing $N^{(A)}$ molecules of component A, $N^{(B)}$ molecules of component B, and so on. The total number of molecules is

$$N=\underbrace{N^{(A)}+N^{(B)}+\ldots+N^{(Z)}}_{N_C\text{terms}} \tag{1}$$

The energy of a molecule i belonging to species A is defined as the sum of its potential energies of interaction with other molecules:

$$u_i=\sum_{\substack{j=1\\ j\neq i}}^{N}\varphi_{i,j} \tag{2}$$

Table 1
Molecular parameters of Ar, Kr, N_2 and CH_4.

Reference	Site	σ (nm)	ε/k_B (K)	Charge (e)
Dougan et al. (2004)	Ar	0.3405	119.8	0
Vermesse and Levesque (1994)	Kr	0.3685	164.4	0
Ravikovitch et al. (2000)	N_2	0.36154	101.5	0
Martin and Siepmann (1998)	CH_4	0.373	148.0	0

where $\varphi_{i,j}$ is the pairwise interaction energy between molecule i and molecule j. The pair energies were calculated from the Lennard-Jones 12-6 potential equation using the molecular parameters in Table 1, their saturation and critical pressures at the temperatures studied are given in Table 2.

The cross molecular parameters are computed from those of pure components with the Lorentz–Berthelot (LB) mixing rules:

$$\sigma_{ij}^{(A,B)}=(\sigma_i^A+\sigma_j^B)/2$$
$$\varepsilon_{ij}^{(A,B)}=\sqrt{\varepsilon_i^A\varepsilon_j^B} \tag{3}$$

In the kMC scheme, the mobility of a molecule i is defined as

$$\nu_i^A=\exp(u_i^A/kT) \tag{4}$$

with u_i^A given by Eq. (2).

If u_i^A is negative, molecule i is in an attractive environment and is less likely to move, than those with positive energies. In the kMC scheme a molecule is moved to a random position according to the Rosenbluth scheme (Frenkel and Smit, 1996) to maintain the stochastic nature of the kMC scheme.

The total mobility of the system is defined as the sum of mobilities of all the molecules:

$$R=\sum_{A=1}^{Nc}\sum_{\substack{i=1\\ i\in A}}^{N^{(A)}}\nu_i^A \tag{5}$$

This is a measure of how fast the system evolves, and the time that the system spends in a given configuration is proportional to:

$$\Delta t=\overline{\Delta t}\ln(1/p)=(1/R)\ln(1/p) \tag{6}$$

where p is a random number $(0<p<1)$. All configurations having the same total mobility R are assumed to follow the Poisson distribution law (Fichthorn and Weinberg, 1991; Battaile, 2008).

We also define the total mobility of a component by summing its mobilities; for example the mobility of component A is

$$R^{(A)}=\sum_{\substack{i=1\\ i\in A}}^{N^{(A)}}\nu_i^A \tag{7}$$

hence

$$R=\sum_{A=1}^{Nc}R^{(A)} \tag{8}$$

2.1.1. The algorithm

In kMC only one move is required: a selected molecule is moved to a random position. The selection is made according to

Table 2
Saturation pressures (P_O) of Ar, Kr, N_2 and CH_4 at the temperatures studied.

Molecule	Temperature (K)	Simulated pressure (atm)				Exp. (atm)
		Gibbs	kMC	Bin-MC	CMC	
Ar	112	6.49	6.86	6.78		7.53 (Miller et al., 1973)
	123	12.57	12.76	12.41		14.0 (Jin et al., 1993)
	148	37.9	39.64	38.08	37.55	43.48 (Schouten et al., 1975)
Kr	148	4.65	5.65	5.63	5.57	5.91 (Schouten et al., 1975)
	177	17.79	19.11	19.28		20.23 (Schouten et al., 1975)
N_2	112	13.53	14.48	14.38		16.19 (Miller et al., 1973)
CH_4	123	2.07	2.63	2.55		2.33 (Jin et al., 1993)

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